

Basic Energy Sciences

FY 2014 Research Summaries



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Cover Images

Left to right beginning on the back cover: **(1)** Ferromagnetic nanostructures (scanning electron microscope image) of MnSi microcrystal grown using chemical vapor deposition. [Image courtesy Oak Ridge National Laboratory] **(2)** Hierarchically porous, graphene-based electrodes for a high-capacity lithium-air battery made of self-assembled functionalized graphene sheets. [Image courtesy Pacific Northwest National Laboratory. Reprinted by permission from Xiao, J., *et al.* 2011. "Hierarchically Porous Graphene as a Lithium-Air Battery Electrode," *Nano Letters* **11**, 5071–78. DOI:10.1021/nl203332e. Copyright 2011: American Chemical Society.] **(3)** Calculated structure of covalently bound thiophene molecules on a methyl-terminated silicon surface. [Image courtesy Joint Center for Artificial Photosynthesis. Reprinted by permission from Yu, M., *et al.* 2013. "Theory of Covalent Adsorbate Frontier Orbital Energies on Functionalized Light-Absorbing Semiconductor Surfaces," *The Journal of Physical Chemistry Letters* **4**, 1701–06. DOI:10.1021/jz400601t. Copyright 2013: American Chemical Society.] **(4)** Scanning tunneling microscope image showing atomically dispersed palladium atoms on a copper surface. [Image courtesy Charles Sykes, Tufts University] **(5)** Tell-tale trail of water's passage left by modified amino acid residues on the way to and from the active site of Photosystem II. [Image courtesy Terry Bricker, Louisiana State University] **(6)** Electron microscope image depicting the emergence of silicon nanostrands from indium droplets (orange spheres) during a plasma-assisted physical vapor deposition growth process. When growth is completed, the nano silicon/indium assembly is used as negative electrodes in lithium-ion batteries. [Image courtesy Argonne National Laboratory] **(7)** Cylinder-forming, self-assembled diblock copolymers (schematic illustration). [Image courtesy Bradley Olsen, Massachusetts Institute of Technology. Reprinted by permission of The Royal Society of Chemistry: From Lam and Olsen 2013.]

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PREFACE

This is a collection of summaries for more than 1200 research projects funded by the Office of Basic Energy Sciences (BES) in Fiscal Year 2014 at some 200 institutions across the U.S. This volume is organized based on the three BES divisions: Materials Sciences and Engineering (MSE); Chemical Sciences, Geosciences, and Biosciences (CSGB); and Scientific User Facilities (SUF). Within the MSE and CSGB divisions, the summaries are further organized by research program. For the SUF division, summaries are provided for the research projects in accelerator physics and x-ray and neutron detectors.

This is the third annual issue of BES research program summaries. The volume covers core research activities supported by BES. While every attempt was made to obtain a summary for each research project supported in FY 2014, there may be some omissions. Some specific activities are not covered, including the construction and operation of scientific user facilities, Energy Frontier Research Centers, the Fuels from Sunlight Energy Hub, the Batteries and Energy Storage Hub, and the Small Business Innovation Research (SBIR)/Small Business Technology Transfer (STTR) program. Each project summary includes: title, point of contact (to whom questions should be addressed), principal investigator, other senior investigators, postdoctoral fellows, graduate students, approximate funding given in FY 2014 (annual funding shows a single year; forward funding shows the entire award period), a brief description of the research project, and research highlights for FY 2014. For Experimental Program to Stimulate Competitive Research (EPSCoR) projects, the funding for the entire award period is shown. Many of these projects are jointly funded by other Department of Energy programs. A small number of awards are jointly funded by more than one BES research program. These entries are duplicated in both research programs and show the full funding amount.

This collection is complementary to the *Basic Energy Sciences 2014 Summary Report*, which describes in detail how BES is structured and managed and provides overviews of each of the three BES divisions and special research activities.

I. CHEMICAL SCIENCES, GEOSCIENCES, & BIOSCIENCES DIVISION

AMO Sciences

Institutions Receiving Grants

Tracing and Controlling Ultrafast Dynamics in Molecules

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Students:	0 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding:	\$140,000 (2014)

PROGRAM SCOPE

The emergence of attosecond technology has shifted our perspective in ultrafast science from the time scales intrinsic to nuclear dynamics to that of electron dynamics. With our projects we seek to provide theoretical support to establish new ultrafast concepts and optical techniques to obtain an advanced understanding and interpretation of electron dynamics in atoms and molecules.

FY 2014 HIGHLIGHTS

1. Finite-range time delays in numerical streaking experiments

The attosecond streak camera technique enables the retrieval of temporal information of ultrafast processes on the attosecond time scale. Based on our quantum simulations as well as a classical trajectory analysis, we have shown that the observed time delay can be written as a sum or integral of piecewise field-free time delays weighted by the instantaneous streaking field strength, relative to the streaking field strength at the instant of transition of the electron into the continuum. This led us to the intuitive interpretation that - for single photoionization - the observed time delay depends on the finite time between the transition of the photoelectron from the initial bound state into the continuum and the end of the streaking pulse.

2. Generation of isolated ultrashort pulses using long driving wavelengths

We have examined an alternative path of generating isolated ultrashort pulses by multi-cycle driving laser pulses at midinfrared wavelengths. Our calculations are based on a numerical model, in which harmonic generation is computed via an extension of the strong-field approximation on the microscopic level. Macroscopically, the gas medium is then discretized into elementary radiators and the radiation (harmonic emission) of each of these sources is propagated to the detector and calculated as coherent sum. Our results indicate, in support of corresponding experimental observations, that a temporal gating of the harmonic emission down to one optical cycle can be achieved.

3. Multiple rescattering dynamics at the single atom level

We have studied a control scheme based on the interrogation of the process of HHG by application of a second color of light. We have demonstrated selective generation of electrons into trajectories

which revisit the parent nucleus several times and have examined the signatures of multiple rescatterings in the temporal and frequency domain of the radiation.

Structure and Dynamics of Atomics, Ions, Molecules and Surfaces

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Uwe Thumm; Kansas State University
Carlos Trallero; Kansas State University
Kevin D. Carnes; Kansas State University
Charles Fehrenbach; Kansas State University
Anh-Thu Le; Kansas State University
Students: 7 Postdoctoral Fellow(s), 22 Graduate(s), 2 Undergraduate(s)
Funding: \$2,500,000 (2014)

PROGRAM SCOPE

A wide range of experimental and theoretical projects have been conducted at the J.R. Macdonald Laboratory (JRML), Kansas State University, which fall into the category of observing and controlling single atoms and molecules on short time scales. The underlying goal is to eventually make this time scale the natural one on which electrons move in matter. These projects revolve around two themes, "Attosecond Physics" and "Control". There is, in reality, no sharp boundary between the two. In fact, we expect considerable cross-fertilization to enrich both efforts. The JRML laser sources, namely the Kansas Light Source (KLS), the newly-installed high power tunable wavelength HITS laser, and the high repetition rate PULSAR, provide a broad range of laser capabilities and ample beam time for research and development. Shorter, more intense attosecond pulses of radiation from harmonic generation, for instance, have been used to investigate electronic motion in the time domain and are constantly being developed further. The JRML theorists continue developing analytical and computational approaches, in addition to building and refining models for complicated processes, to analyze the interaction of femto- and atto-second pulses of light with atoms, molecules, and surfaces. Most JRML group members additionally participate in experiments in various labs around the world, provide theoretical support for such experiments, and otherwise actively pursue collaborations outside of JRML. Moreover, JRML continues to host several outside investigators for their experiments. All of these activities build towards the ultimate goal of understanding the dynamical processes of reactions well enough to control them while positioning JRML to be a leading center for ultrafast AMO physics.

FY 2014 HIGHLIGHTS

The Lab has seen many upgrades during this year. One of the more significant is the addition of a world-class 1 kHz ultrafast intense laser system funded partly by DOE. The HITS laser, which was delivered and installed by KMLabs in the spring, is rapidly being incorporated into our research, extending our capabilities by providing higher pulse energy (20mJ), tunable mid-IR wavelengths using a white-light-seeded optical parametric amplifier, and long term (better than 300 mrad RMS over 9 hours) carrier-

envelope phase (CEP) stability. We have been involved in a variety of projects this past year. Some of the most significant are: Imaging charge transfer in iodomethane upon x-ray photoabsorption, waveforms for optimal sub-keV high-order harmonics with synthesized two- or three-color laser fields, sub-femtosecond steering of hydrocarbon deprotonation through superposition of vibrational modes, Optical damage threshold of Au nanowires in strong femtosecond laser fields, multi-pulse three-dimensional alignment of asymmetric top molecules, and enhancing the intense field control of molecular fragmentation.

Probing Complexity using the LCLS and the ALS

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Funding: \$630,000 (2014-2016)

PROGRAM SCOPE

The goal of our research program is to investigate fundamental interactions between photons and molecular systems to advance our quantitative understanding of electron correlations, charge transfer and many body phenomena. Our research investigations focus on probing on femtosecond time-scale multi-electron interactions and tracing nuclear motion in order to understand and ultimately control energy and charge transfer processes from electromagnetic radiation to matter. Most of our work is carried out in a strong partnership with theorists. Our current interests include: 1) The study of non-linear and strong field phenomena in the x-ray regime using free electron lasers (FELs), and in particular, the ultrafast linac coherent light source (LCLS) x-ray FEL facility at the SLAC National Laboratory. 2) Time-resolved investigations of molecular dynamics using pump-probe techniques. Our experiments probe physical and chemical processes that happen on femtosecond time scales. This is achieved by measuring and examining both electronic and nuclear dynamics subsequent to the interaction of molecules and clusters with LCLS pulses of various fluence and fs (4-500) pulse duration. 3) The study of dynamics and correlated processes in select molecules as well as anions with vuv-soft x-rays from the Advanced Light Source (ALS) at Lawrence Berkeley Laboratory.

FY 2014 HIGHLIGHTS

1) Buckyball Explosion by Intense Femtosecond X-Ray Pulses: A Model System for Complex Molecules. We have carried out an experimental and theoretical study of C₆₀ molecules interacting with intense x-ray pulses from the LCLS X-ray free electron laser, revealing the influence of processes not previously reported. This work presents an essential step for the rigorous, quantitative understanding of femtosecond molecular dynamics. Measurements guided the development of molecular dynamics simulations suitable for large molecules exposed to intense XFEL pulses. Experimental and simulation data on C₆₀ ion dynamics reveal that a complex variety of physical and chemical processes are present in these interactions. Our model demonstrates that full atomic fragmentation of C₆₀ occurs at the highest fluence while molecular fragments are generated at medium fluence. We show that ionization suppression occurs for very short pulses (4 fs). Furthermore, our experiment provided evidence that the charged particles produced by exposing an extended quantum system, C₆₀, to high-fluence x-rays behave as if they were classical particles. At high fluence, the parent molecule explodes within few tens

of fs, giving rise to fragment ions and highly charged state of C atom including fully stripped C fragments. Scientific American, 310, 64, (2014); Nature Comm., 5, 4281 (2014); Faraday Discuss. 171, 471 (2014); J. Phys. B: At. Mol. Opt. Phys. 47 124006 (2014); J. Elec. Spect and Rela. Phen, 196, 34 (2014).

2) Advanced Instrumentation for LCLS-Based Research. We have built and commissioned a multi-user facility that consists presently of two instruments located at the LCLS and available to any user. They are: 1) the X-Ray Split and Delay (XRSD) to carry out time-resolved experiments utilizing x-ray pump x-ray probe technique and 2) the LAMP instrument which presently houses two imaging detectors and two VMI spectrometers. These instruments have already been used for experiments.

EARLY CAREER: Ultrafast Electron Diffraction from Aligned Molecules

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Funding: \$150,000 (2014)

PROGRAM SCOPE

The aim of this project is to record time-resolved electron diffraction patterns of aligned molecules and to reconstruct the 3D molecular structure. This will allow us to investigate, on a fundamental level, the conversion of light into mechanical and chemical energy at the molecular level. Femtosecond laser pulses are used to excite the molecules and to align them, and an electron pulse is used to record the structure at a specific time after the interaction with the laser. The molecular alignment increases the information content of the diffraction patterns, and allows for retrieval of 3D structures. This method will allow for capturing structures of intermediate states in ultrafast photoreactions with sub-Angstrom spatial resolution.

FY 2014 HIGHLIGHTS

In this past year, we have experimentally investigated the interaction of a strong femtosecond laser pulse with molecules in order to determine the limits of the impulsive laser alignment method. We have investigated the effect of laser pulses using a linear molecule, carbon disulfide. It was observed that the degree of alignment increases with laser intensity until it reaches a saturation at an intensity below the ionization threshold. At intensities beyond the saturation level there is a deformation of the molecular structure. Using ultrafast electron diffraction we can characterize the structural changes with sub-Angstrom spatial resolution, and we were able to characterize the alignment, deformation and breakup of the molecules as a function of laser intensity. While we had previously shown that 3D structures of symmetric top molecules can be retrieved from diffraction patterns of aligned molecules, we have now extended the retrieval algorithm to work also for asymmetric molecules. We achieved this by using a two-step retrieval process. In the first step, two diffraction patterns are combined using a genetic algorithm to recreate a diffraction pattern corresponding to perfect 1D alignment. In the second step, we use an iterative phase retrieval algorithm that works with multiple cylindrical harmonics to retrieve the position of the atoms. We have successfully tested the algorithm with simulated diffraction patterns of trifluorotoluene ($C_6H_5CF_3$), an asymmetric molecule.

Atomic and Molecular Physics in Strong Fields

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Funding: \$115,000 (2014)

PROGRAM SCOPE

In this research program, we address the fundamental physics of the interaction of atoms and molecules with intense ultrashort laser fields. The main objectives are to develop new theoretical formalisms and accurate computational methods for *ab initio* nonperturbative investigations of multiphoton quantum dynamics and very high-order nonlinear optical processes of one-, two-, and many-electron quantum systems in intense laser fields, taking into account detailed electronic structure information and many-body electron-correlated effects. Particular attention will be paid to the exploration of the effects of electron correlation on high-harmonic generation (HHG) and multiphoton ionization (MPI) processes, multi-electron response and underlying mechanisms responsible for the strong-field ionization of atoms, and diatomic, and small polyatomic molecules, time-frequency spectrum, and coherent control of HHG processes for the development of shorter and stronger attosecond laser pulses, etc.

FY 2014 HIGHLIGHTS

The major research highlights of our DOE project in 2014 are briefly summarized as follows: (1) Coherent Phase-matched VUV Generation by Field-controlled Bound States. Recently in collaboration with the experimental group led by Dr. Z. Chang in UCF, we extend our self-interaction-free TDDFT and generalized Floquet formalism and uncover a new regime of phase-matched below-threshold harmonics generation, for which the generation and phase matching is enabled only near Stark-shifted resonance structures of the atomic target. This work opens the door to the future development of compact, high flux and ultrafast VUV light sources without the need for cavity or nanoplasmonic enhancement. (2) Sub-optical-cycle HHG Dynamics and Ultrafast Spectroscopy in the Attosecond Time Domain. We performed the first *ab initio* study of the subcycle HHG dynamics of He atoms in near-infrared (NIR) laser fields subject to excitation by a single extreme ultraviolet (XUV) attosecond pulse (SAP). We explored the dynamical behavior of the subcycle high harmonic generation (HHG) for transitions from the excited states to the ground state and found oscillation structures with respect to the time delay between the SAP and NIR fields. Our analysis reveals several novel features of the subcycle HHG dynamics and we identify the mechanisms responsible for the observed peak splitting in the photon emission spectra. (3) Subcycle Transient Structures in Time-Dependent Multiphoton-Ionization (MPI) Rate. We perform an accurate exploration of the subcycle transient MPI dynamics of atomic and molecular systems subject to intense near-infrared laser fields on the subfemtosecond time scale. MPI bursts within a single optical cycle are found in the time-dependent ionization rates. The analysis of the electron density reveals that several distinct density portions can be shaped and detached from the target within a half cycle of the laser field.

Formation of Ultracold Molecules

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Funding: \$102,000 (2014)

PROGRAM SCOPE

The main aims of this Research Program are to identify efficient approaches to obtain ultracold molecules, and to understand their properties. To that end, we often need to calculate the electronic properties (energy surfaces, dipole and transition moments, ro-vibrational states, etc.), as well as the interaction of the molecules with their environment (surrounding atoms, molecules, or external fields).

FY 2014 HIGHLIGHTS

We have made progress on 4 main axes of research: 1) Rydberg interactions: we have recently started to investigate how interactions can be affected by dressing atoms with a Rydberg state. We have shown that Rydberg-dressed interactions could be used to tune ultracold chemical reactions. We illustrated the concept with benchmark system, namely $H_2+D \rightarrow HD+H$. We also investigate a possible new chemical bound between ground state atoms using Rydberg dressing of the atoms. The molecular bound states would be extremely long-range, roughly 500 bohr radii, and very weakly bound. 2) Energy surfaces and reactions: We recently computed the surfaces for $RbOH^-$ and $RbOH$ to model the associative detachment reaction, paying special attention to the angular dependence of the Potential Energy Surface (PES). We also extended our study of atom-diatom reactive scattering to H_2+Cl to investigate the effect of resonances near the scattering threshold. We found a new universal behavior of the inelastic cross section in the s-wave regime scaling as $1/k^3$, which can be explained by the proximity of a pole in the complex k-plane. Finally, we are in the process of completing the computation of PES of two other systems: Mg^{+2} and Sr^{+2} . More recently, we helped analyzing experimental results on $NaCa^+$. 3) Long-range interaction between diatomic molecules: We summarized some of our previous work in a book chapter on ultracold molecules for quantum information processing. 4) Formation of dimers and tetramers: We recently started to explore how Feshbach resonances could enhance the pump-dump scheme to produce ground state molecules, and we are using the same approach to investigate the possible formation of tetramers. In fact, by controlling the long-range interaction between polar diatomic molecules using external DC electric field, we could increase the shorter-range overlap of the continuum and excited states (as in FOPA: Feshbach Optimized Photo-Association), and thus the formation rate of tetramers.

Optical Two-Dimensional Spectroscopy of Disorder Semiconductor Quantum Wells and Quantum Dots

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Funding: \$120,000 (2014)

PROGRAM SCOPE

We are using two-dimensional coherent spectroscopy to study electronic excitations, mainly excitons, in semiconductor nanostructures. During the next grant period, we plan to focus on using the ability of 2D coherent spectroscopy to make size resolved measurements in an ensemble sample to study size dependent phenomena in epitaxially grown self-organized quantum dots and in colloidal quantum dots. Typically the size dependence can only be determined by making a series of single dot measurements, whereas it can be extracted from a single two-dimensional spectrum. In addition, two-dimensional coherent spectroscopy can measure energetic shifts and splittings that are small compared to the inhomogeneous width, as long the fluctuations in the energies are correlated. In the self-organized InAs dots, we will use 2D coherent spectroscopy to 1) study the exciton-phonon interactions of both the ground-state and excited state transitions, 2) study the coherent and incoherent interaction between the ground-state and excited-state transitions and 3) to observe Rabi flopping due to a prepulse. We plan to use two-dimensional coherent spectroscopy to study three types of colloidal quantum dots. For CdSe/ZnS dots we will study the low temperature dephasing to determine underlying physical mechanism. For Ge dots we will determine the excitonic dephasing time, the fine structure and the biexciton binding energy. In PbSe/CdSe dots, we will make similar measurements. Both the Ge and PbSe/CdSe dots are quite new, thus very little is known about them, so these measurements will help establish their properties. In addition both are technologically relevant for solar energy applications.

FY 2014 HIGHLIGHTS

During the most recent grant period we used two-dimensional coherent spectroscopy to 1) measure the size dependence of the biexciton binding energy in self-organized InAs quantum dots, 2) observe contributions due to the $\chi^{(5)}$ terms and trions in the same sample, 3) measure the dephasing of excitons in 110 oriented GaAs quantum wells, 4) observe many-body induced coupling in asymmetric InAs double quantum wells, 5) observe exciton-trion coupling in an n-doped CdTe quantum well and 6) make preliminary measurements of the low-temperature dephasing of CdSe/ZnS colloidal quantum dots.

Understanding and Controlling Strong-Field Laser Interactions with Polyatomic Molecules

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Funding: \$150,000 (2014)

PROGRAM SCOPE

When intense laser fields interact with polyatomic molecules, the energy deposited leads to fragmentation, ionization and electromagnetic emission. The objective of this project is to determine to what extent these processes can be controlled by modifying the phase and amplitude characteristics of the laser field according to the timescales for electronic, vibrational, and rotational energy transfer. Controlling these processes will lead to order-of- magnitude changes in the outcome from laser-matter interactions, which may be both of fundamental and technical interest. The proposed work is unique because it seeks to combine knowledge from the field of atomic-molecular- optical physics with knowledge from the fields of analytical and organic ion chemistry. This multidisciplinary approach is

required to understand to what extent the shape of the field affects the outcome of the laser-molecule interaction and to which extent the products depend on ion stability. The information resulting from the systematic studies will be used to construct a theoretical model that tracks the energy flow in polyatomic molecules following interaction with an ultrafast pulse.

FY 2014 HIGHLIGHTS

This year we developed two different methods for determining electronic coherence in large molecules in solution using shaped laser pulses. These findings will eventually speed up and make possible single molecule coherent spectroscopies. Two publications have resulted from this work and a third one is pending. We completed a significant theory/experiment collaborative project on the behavior of polyatomic molecules under intense femtosecond laser irradiation. These findings are now published as a Feature Article in the Journal of Physical Chemistry. We have been completing a project on the study of electronic coherence mediated quantum control of chemical reactions in polyatomic molecules.

Production and Trapping of Ultracold Polar Molecules

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Students: 1 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding: \$135,000 (2014)

PROGRAM SCOPE

Our goals are to produce and trap a gas of polar molecules in the ultracold regime, and to study novel physical effects associated with the low temperatures and/or the polar nature of the molecules. Using the technique of photoassociation, we form RbCs molecules by binding together laser-cooled Rb and Cs atoms. We previously created a gas of rovibrationally-excited RbCs in an optical trap, and studied the collisional properties of the molecules. Our focus since has been on the production of RbCs molecules in their absolute rovibronic ground state, where they will be stable against inelastic collisions and hence suitable for precisely controlled study and manipulation. Once a large trapped sample is formed, we will study chemical reactions at ultracold temperatures, dipolar effects in collisions, and similar phenomena.

FY 2014 HIGHLIGHTS

In Fiscal Year 2013, we have continued our study of a recently-discovered, simple method to produce ultracold RbCs in its absolute ground state. We drive photoassociation (PA) transitions from free Rb and Cs atoms into tightly-bound RbCs molecular states that can decay to the absolute ground state. We observe high rates of formation of RbCs into low-lying vibrational levels, including the vibrational ground state, through intermediate PA resonances that are well-characterized from previous spectroscopy. In the latest Fiscal Year, we used a new high-resolution spectroscopic technique to measure the distribution of rotational levels formed via PA. With this data, we were able to further characterize the decay process that leads to formation of ground state molecules. We also verified that, as expected, a large fraction ($\sim 1/3$) of the vibrational ground state molecules are formed also in their rotational ground state. We have subsequently gone on to apply this method to form molecules in an optical trap, and to verify that we are trapping significant numbers of ultracold, rovibrational ground-state molecules, as has

long been our goal. We have now begun to study the collisional properties of these absolute ground-state RbCs molecules. RbCs in its ground state should be immune to inelastic collisions with itself and with Cs atoms. Hence, molecule production in the presence of dense Cs vapor should make it possible to use Cs atoms as a “scrubber” to remove, via inelastic collisions, residual rovibrationally-excited RbCs molecules that otherwise would accumulate in the trap. We are exploring the dynamics of the scrubbing process in an optical trap now.

Attosecond Ultra-Fast X-Ray Science

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Funding: \$500,000 (2014-2015)

PROGRAM SCOPE

The new frontier of attophysics aims at visualizing and controlling in real time the motion of electrons composing matter. In the new millennium the generation of attosecond XUV pulses became a laboratory reality. A primary goal of this grant is to apply these light pulses in a series of time-resolved experiments in order to understand correlated electron dynamics, and by doing so provide a new perspective on elementary atomic processes. These studies will be enabled by the unique technology developed at The Ohio State University (OSU) for attosecond science that utilizes long wavelength lasers and the OSU attosecond beamline/end-station. Several key attosecond measurements were achieved in the previous grant cycle and provide a firm foundation for continued progress in the renewal. A second thrust will continue to explore fundamental aspects of high harmonic generation and the ability to utilize this spectroscopy to access some fundamental atomic parameters. The second scope of this grant is the continued implementation of AMO science program using the ultra-fast, intense x-rays available at LCLS XFEL. The objective is the study of fundamental atomic processes involving multiple inner-shell ionization, x-ray nonlinear optics and the development of unique methods for time-resolved x-ray physics. These investigations will also enable novel metrological methods for the characterization of the LCLS beam and the foundation for understanding more complex matter-x-ray interactions, e.g. biological imaging. In addition this grant allows the development of experimental and intellectual competency using different 4th generation platforms whether on laboratory attosecond sources or the larger facilities available at the LCLS. The OSU program has already trained graduate students and post-doctoral research associates that are now contributing to x-ray science as staff members at DOE laboratories.

FY 2014 HIGHLIGHTS

Attosecond pulse shaping around a Cooper minimum. One signature of atomic structure, first discussed by Cooper, is a local minimum in the photoionization (PI) probability at a specific photon energy. This Cooper minimum (CM) is caused by a sign change, equivalent to a π -phase jump, in the bound-free transition dipole of one angular momentum channel. The CM has been extensively studied using traditional photoionization spectroscopy but the phase of the total transition dipole is not directly accessible, although it strongly influences the measured electron angular distribution and spin polarization. Consequently the Cooper minimum in argon became an excellent candidate for examining the viability of high harmonic spectroscopy. We have investigated the phase modification in the high

harmonic emission induced by the 3p Cooper minimum of argon, over a wide spectral range. In the experiment, the derivative of the spectral phase, the group delay (GD), is measured using the resolution of attosecond beating by interference of two-photon transitions (RABBITT) method. The measured RDM phase and amplitude agrees well with predictions based on the scattering phases and amplitudes of the interfering s- and d-channel contributions to the complementary photoionization process.

RABBITT measurement and the interpretation of the Wigner delay in photoionization. Photoionization by an XUV attosecond pulse train in the presence of an infrared pulse (RABBITT method) conveys information about the atomic photoionization delay. By taking the difference of the spectral delays between pairs of rare gases (Ar,He), (Kr,He) and (Ne,He) it is possible to eliminate in each case the larger group delay (“attochirp”) associated with the attosecond pulse train itself and obtain the Ar, Kr and Ne “effective” Wigner delays referenced to calculated He delay. Our extracted delays have been compared with several theoretical predictions and the results are consistent within 30% as over the energy range.

Spatial - Temporal Imaging during Chemical Reactions

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Sr. Investigator(s): Pierre Agostini; Ohio State University
Students: 1 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding: \$222,000 (2014)

PROGRAM SCOPE

This grant is an experimental program designed to develop and demonstrate the tools for directly “watching and clocking” both the nuclear and the electronic motion during chemical bond making/breaking and other comparable processes. Our program is built around two facets of the molecule self-probing paradigm, derived from the strong-field rescattering model scaled to long wavelength. The first one is laser-induced electron diffraction in which the molecular structure is retrieved from the photoelectron momentum distribution with sufficient space-time resolution to observe the motion of the nuclei as directly as conventional electron diffraction measures equilibrium nuclear positions. The second is based on high harmonic generation from aligned molecules and the tomographic reconstruction of the Dyson orbitals pushed to higher precision by virtue of our mid-infrared driver lasers, combined with a pump-probe scheme. Both approaches will be benchmarked and applied to the resolution of unimolecular dissociation reactions. Both techniques allow us to exploit fundamental principles of strong-field scaling and combined they have the potential to visualize both the nuclear and electronic dynamics in chemical and material processes.

FY 2014 HIGHLIGHTS

In Nature Communication we introduced fixed-angle broadband laser-driven electron scattering (FABLES) as an alternative to fixed-energy, angle-swept LIED. FABLES is analogous to white light interferometry in optics, and this is the first experimental confirmation that broadband electron wave packet (EWP) can be used for imaging. In FABLES, the energy-dependent DCS is retrieved as compared to the angle-dependent DCS of the LIED method. The main benefit of FABLES is a trivial retrieval of molecular structure via a simple Fourier transform (FT) with no theoretical fitting or modeling, e.g. no *a priori* knowledge of laser ionization. Furthermore, the method “visualizes” only bonds parallel to the laser polarization and has the potential for routine, real-time imaging in a pump-probe configuration.

This unique aspect combined with molecular alignment was shown theoretically to offer a full molecular tomographic reconstruction.

High Intensity Femtosecond XUV Pulse Interactions with Atomic Clusters

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Students: 0 Postdoctoral Fellow(s), 5 Graduate(s), 0 Undergraduate(s)
Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

The goals of our experiments are to extend experiments on the explosion of van der Waals bonded atomic and molecular clusters irradiated at 800 nm to the short wavelength regime (1 to 50 nm). Our studies with XUV light are designed to illuminate the mechanisms for intense pulse interactions in the regime of high intensity but low ponderomotive energy by measurement of electron and ion spectra. This regime is very different from the IR where the ponderomotive potential is significantly greater than the binding potential of electrons in the cluster. We perform these studies by converting a 1.5 J, femtosecond laser to short wavelengths by high order harmonic generation (HHG) in a gas jet. We are working to confirm a hypothesis about the origin of the high charge states seen in XUV irradiated exploding clusters. We assessed from our first experiments that the photo-ionization of the atoms and ions in each cluster is strongly affected by plasma continuum lowering (ionization potential depression) in a cluster nano-plasma. This effect, which is well known in plasma physics, leads to a depression of the ionization potential enabling direct photo-ionization of ion charge states which would otherwise have ionization energies which are above the photon energy employed in the experiment. In our present work, we intend to confirm this hypothesis by performing experiments in which XUV pulses of carefully chosen wavelength irradiate clusters composed, on one hand, of only low-Z atoms and, on the other hand, clusters with a mixture of this low-Z atom with higher Z atoms. The latter clusters will exhibit higher electron densities and will see greater ionization potential lowering than in the clusters composed only of low Z atoms. By measuring the charge state distribution, we can see if direct single photon photo-ionization channels open for higher charge states when there is a higher plasma density in the cluster.

FY 2014 HIGHLIGHTS

We completed the characterization of a long focal length, HHG beamline on a 1.5 J, 30 fs, 10 Hz Ti:sapphire laser. This new beam has produced XUV laser pulse energies at 38 nm which are twenty times that of our previous experiments. We made direct comparison of ion charge states observed in large Xe clusters in the new apparatus. We observed a dramatic drop in ion intensities above Xe⁶⁺ as observed previously. With the higher XUV intensity now available we see production up to Xe¹¹⁺ in the new experiments compared with Xe⁸⁺ in previous ones. We have also completed the measurement of ion charge state distributions, ion energies, and the electron emission spectra in Xe, Ar, N₂, CH₄, and Xe doped CH₄ clusters formed in a cryo-cooled, supersonic cluster source in the new target chamber. Some of the new clusters measured can be compared directly with experiments previously complete using the LCLS laser at much shorter wavelengths. We have now tested the LAM production of clusters of Ag on a

source which will be soon mounted on the new target chamber. We will then study ion production from XUV pulses in oxide clusters (like SiO₂ and SnO₂).

Atomic and Molecular Electron Correlation in Strong Fields

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Funding: \$100,000 (2014)

PROGRAM SCOPE

We are interested to understand how very intense and very short laser pulses excite electrons in atoms and molecules, with intensities in the range above one-tenth PW per square centimeter. The combination of phase-coherent character and short-time nature of laser pulses in related experimental use creates substantial challenges to theoretical study in this domain. The intensities are high enough to mandate development of non-perturbative approaches. We have discussed the theoretical successes and listed the still-existing challenges in a recent article in *Reviews of Modern Physics*. Challenging complications of great interest arise when more than one electron is dynamically active in response to the laser excitation.

FY 2014 HIGHLIGHTS

In the current grant year we have undertaken two projects. First, we will extend the method we introduced last year that combines quantum and classical time-dependent descriptions of atomic electron evolution, labeled the SENE approach. The goal is to overcome the extreme demands made on computational resources by more conventional methods. Second, we have begun to calculate the degree of electron-electron correlation that develops during short-pulse ionization. Our method will allow the first distinction to be made between classical and quantum origins of correlation, a question of fundamental interest for which no answers are currently known.

Image Reconstruction Algorithms

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Students: 0 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

Digital image processing has played a significant role in microscopy for decades. Removing noise, enhancing contrast, identifying features and constructing 3D models are now routine operations that the microscopist relies on to extract the maximum information from his instrument. These now standard forms of data manipulation are in a sense refinements in that they begin with something that

is already recognizable as an image. However, with the development of techniques such as diffractive imaging the scope of digital processing in microscopy has expanded considerably. The data delivered by the new instruments are often very indirectly related to actual images and sophisticated algorithms are increasingly an integral component of the actual microscope. One of the most ambitious plans for algorithmically enabled microscopy is the proposal to image individual biological particles such as proteins and viruses with X-ray free electron lasers. The incentive for the development of this capability is strong, given that many of the most interesting targets of study resist crystallization, the necessary first step in the standard crystallographic approach to structural biology. But while the brilliance of free-electron lasers such as LCLS is higher by orders of magnitude than synchrotron sources, so too is the amplification effect of crystals. Single-particle imaging at LCLS will not only be very indirect, as diffraction images, but extremely noisy because of the weak signal. The main project described in this proposal is the further development of the expand-maximize-compress (EMC) algorithm for obtaining 3D structure from millions of noisy diffraction data. This algorithm has been very successful in simulations, at building accurate models in the standard setting where the particle orientation is unknown in each frame of data. The new studies will address various forms of background in the data and assess the effects of particle heterogeneity.

FY 2014 HIGHLIGHTS

No FY14 Highlights received.

Collective Coulomb Excitations and Reaction Imaging

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Funding: \$96,000 (2014)

PROGRAM SCOPE

Innovations in few-body science at molecular nano levels will be a critical component of ongoing international efforts to establish sustainable environmental and energy resources. The varied research paths to be taken will require the development of basic science on broad fronts with increasingly flexible views to crossover technologies. Although the work described and performed in this project is theoretical, our interest in these topics remains motivated by the recent surge in and success of experiments involving few-body atomic and molecular fragmentation and the collection of all the fragments. We accordingly continue two parallel efforts with (i) emphasis on reaction imaging while (ii) pursuing longtime work on collective Coulomb excitations. As in the past, we continue to place priority on research relevant to experiment.

FY 2014 HIGHLIGHTS

Three papers have been published this past year as a culmination of efforts on this project to track the origins of classical trajectories in an otherwise fully time-independent quantum reaction event. In the first of these papers, we have analyzed the so-called imaging theorem (IT) to establish an asymptotic relation for macroscopic times between coordinate and momentum wavefunctions describing the

many-particle state of an arbitrary fragmentation reaction. In the second paper, we extended the IT to electric- and magnetic-field extraction and position-sensitive detection as widely used in modern reaction microscopes. In the third paper, we derived a multi-fragment generalization of the IT and emphasized an alternative point of view relevant to quantum imaging that fully establishes a link to the classical trajectories without wavepackets or wavefunction collapse.

Studies of Autoionizing States Relevant to Dielectronic Recombination

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Funding: \$148,000 (2014)

PROGRAM SCOPE

In this DoE sponsored program we have worked on two major areas. The first is understanding the response of atoms to simultaneously applied low and high frequency fields which are harmonically related. Experiments done with a combined xuv attosecond pulse train (APT) and an intense infrared laser field showed a clear phase dependence of the ionization of He atoms on the phase of the infrared field at which the attosecond pulses arrived. The phase dependence arises because the energy transfer from the low frequency field to the He electron excited by the APT depends on the phase of the infrared field at which the excitation occurs. The accompanying theoretical analysis showed that the magnitude of the phase dependent signal depended on the coherent effect of the train of attosecond pulses. We are conducting analogous experiments having using a microwave field as the low frequency field and a near infrared laser as the high frequency field. With previous DoE support we used a single ps infrared laser pulse which could be moved temporally relative to the microwave field. We were able to observe a clear dependence on the phase of the microwave field at which the ps pulse, but the signal was very small, less than 0.1%. The present effort has been focused on extending our work to match the APT, as opposed to a single attosecond pulse. We have replaced the ps infrared laser with two diode lasers whose beat note is phase locked to the second harmonic of the microwave source generating the microwave field. The two lasers generate a 100% amplitude modulated infrared field, analogous to the APT, which has maxima every half microwave cycle. These maxima can be phase shifted relative to the microwave field, mimicking the APT and the near infrared laser. If the coherent effect of the multiple pulses in an APT is important we should see a corresponding increase in the magnitude of the phase dependent energy transfer signal. The second area in which we have worked is to measure

FY 2014 HIGHLIGHTS

The most striking advance was that we observed phase dependent energy transfer using our amplitude modulated laser, which was phase locked to the microwave field. Unlike the single ps infrared pulse, the magnitude of the phase dependent signal was enormous, 10%. This observation verified the theoretical claim that the coherent effect of the APT was important in the earlier experiments. Depending on how we tune the frequencies of the diode lasers we are able to see the transfer of population to both higher and lower energy, as expected theoretically. In much of the literature on the interactions of strong electromagnetic fields with atoms or molecules the coulomb potential is ignored. While this approximation is excellent in some cases, in problems involving near threshold electrons it is wrong, as

these experiments clearly demonstrate. We have completed a series of microwave measurements of the intervals between the high angular momentum states of Ca. Ca^+ is a most promising candidate for an optical clock, and its dipole polarizability was not known to 10%. Our experimental value for the dipole polarizability of Ca^+ is in good agreement with the recently calculated value, providing confidence that the black body radiation shift can be calculated with sufficient accuracy to correct for temperature shifts of the clock. The Ca^+ clock transition has a measurement uncertainty of 1 Hz, and the black body shift at 300K is 0.4 Hz. Since the shift has a T^4 temperature dependence, the temperature shift is quite important. While our value of the dipole polarizability agree with the calculations, the quadrupole polarizability does not, although the source of the discrepancy is not apparent. If it can be identified, we shall be able to extract more precise values from our measurements.

Experiments in Ultracold Molecules

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Students: 0 Postdoctoral Fellow(s), 3 Graduate(s), 0 Undergraduate(s)
Funding: \$125,000 (2014)

PROGRAM SCOPE

This project is currently focused on the production of molecules at sub-millikelvin temperatures via the process of photoassociation. Our experiments begin with ultracold Rb atoms confined at high density in a magneto-optical trap. We then apply pulses of frequency-chirped light to form excited-state molecules by long-range photoassociation of the colliding atoms. Normally, ground-state molecules are produced by spontaneous emission of these excited molecules. However, by manipulating the frequency and amplitude of the pulses on the nanosecond time scale, we can coherently control the molecular formation process. The resulting ground-state molecules are detected using state-selective ionization with a pulsed dye laser. In conjunction with the molecular experiments, we are developing the technology to enable production of pulses and frequency chirps on nanosecond and subnanosecond time scales. Diode laser light is manipulated by fiber-optic-based electro-optical phase and intensity modulators that are driven by a fast arbitrary waveform generator. The resulting chirped pulses are then amplified by a tapered semiconductor amplifier or by injection locking a slave diode laser. The output pulses are diagnosed using heterodyne analysis. Overall goals of the program include the development of techniques to control the interactions of ultracold atoms, improved schemes for ultracold molecule production, and application of the techniques of coherent control to ultracold systems. Ultracold molecules have many potential uses, including precision measurements, quantum degeneracy, quantum computing and ultracold chemistry. Understanding, controlling, and optimizing their formation is important to many of these applications.

FY 2014 HIGHLIGHTS

We have extended our work on the production of ground-state rubidium molecules with frequency-chirped light. We previously found a dramatic difference in the production rate for positive and negative chirps and identified, via quantum simulations, the mechanism for this difference. The formation of ground-state molecules takes place in two-steps. First, a colliding pair of atoms absorbs a photon and forms an excited molecule. Then, this excited state makes a transition to the ground state, either by

incoherent spontaneous emission or by coherent stimulated emission. For the coherent process, a positive chirp provides the proper time ordering of the two steps and thus enhances the formation rate. We are currently using faster chirps and shorter pulses, as well as higher intensities, in order to enhance the coherent contribution and diminish the role of spontaneous emission. We are also implementing a novel double-pass configuration with a tapered semiconductor amplifier in order to achieve even higher intensities of the chirped light.

Physics of Correlated Systems

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Sr. Investigator(s):
Students: 2 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding: \$145,000 (2014)

PROGRAM SCOPE

The focus of this project is the theoretical quantum mechanical description of systems having two or more strongly coupled degrees of freedom. While diverse topics come under investigation, the unifying theme connecting all of the supported research is the goal of overcoming existing limitations in the quantitative and qualitative understanding of nonperturbatively interacting atomic and molecular systems, in which energy and angular momentum is exchanged between different coordinates or modes of the system. We have continued our efforts in recent years to understand the interaction of very short pulsed lasers with atomic and molecular systems. A second thrust is in the area of electron-molecule collisions, where there are frequently strong correlations between the incident electron motion and other electrons in the molecular target, or with the nuclear motion degrees of freedom. In one new direction for this project, we have begun an investigation into the connection between quantal and classical theories of three-body recombination in collisions of three neutral atoms. The resulting sharper understanding of the borderline between quantal and classical regimes has led to the realization that ion-atom-atom three-body recombination can be accurately treated using the techniques developed for collisions of three neutral atoms. These systems are all representative of nonperturbative energy transfer processes, in the sense that energy from one degree of freedom becomes coupled or transformed into another degree of freedom in a microscopic system. Another area of continuing development has been an extension and application of theoretical techniques that allow a systematic separation of short-range interaction effects and long-range evolution of a fragmented quantum system.

FY 2014 HIGHLIGHTS

Three-body recombination and its time-reversed process have historically been some of the most difficult types of energy transfer processes to describe using the standard toolkits of theoretical atomic and molecular physics. Our project has made strides over the years in advancing this theoretical capability, and the past year has seen encouraging progress in extending the range of systems for which three-body recombination processes such as $A+B+C \rightarrow AB+C$ can be quantitatively described. Calculations this year have helped to delineate the energy range above which classical Newtonian methods can be safely utilized instead of the far more expensive and complicated quantal treatments that are required in the low energy limit. A new direction that followed up this better understanding has been an initial treatment of three-body recombination processes for which one of the three incident

collision partners is ionized. This has already generated some encouraging results such as the classical threshold law for this process, apparently not previously derived. Further extensions to four interacting atoms have been of interest for some time, although the computational capabilities are far more limited for the four-body problem than they are for three-body systems. As a prototype four-body system, we have conducted a first exploration of the positronium dimer molecule, consisting of two positrons and two electrons. This intriguing system has some of the same topological features as the hydrogen molecule, such as a mix of ionized and neutral fragmentation channels, but with a mass ratio that makes the usual Born-Oppenheimer picture inappropriate. Our study has shown the feasibility of developing a coupled-channels hyperspherical representation of dynamical processes such as charge exchange. Finally, progress has been achieved this year in reformulating the frame transformation theory of photoionization microscopy for a nonhydrogenic atom in an external electric field.

Using Strong Optical Fields to Manipulate and Probe Coherent Molecular Dynamics

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Principal Investigator: Robert Jones
Sr. Investigator(s):
Students: 1 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding: \$145,000 (2014)

PROGRAM SCOPE

This project focuses on the exploration and control of dynamics in atoms and small molecules driven by strong laser fields. Our goal is to exploit strong-field processes to implement novel ultrafast techniques for manipulating and probing coherent electronic and nuclear motion within atoms, molecules, and on surfaces. Ultimately, through the application of these methods, we hope to obtain a more complete picture of correlated multi-particle dynamics in molecules and other complex systems.

FY 2014 HIGHLIGHTS

During the current funding year we have: (i) continued our investigation of transient, field-free orientation of polar molecules induced by combinations of intense optical and THz pulses; (ii) extended our studies of strong-field ionization by intense single-cycle THz pulses, moving from Rydberg atom targets to nano-structured metals; (iii) examined the role of multi-electron dynamics in enhanced multiple-ionization of diatomic molecules; and (iv) begun a collaboration with the DiMauro/Agostini group at the Ohio State University to characterize the influence of the electronic binding potential on energy transfer between an optical dressing field and near-threshold attosecond photo-electrons.

Molecular Dynamics Probed by Coherent Soft X-rays

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Funding: \$300,000 (2014)

PROGRAM SCOPE

The goal of this project is to develop novel short wavelength probes of molecules and nanosystems, and to understand the response of atoms and molecules to strong laser fields, in particular mid-infrared (mid-IR) laser fields. Several recent breakthroughs from the Kapteyn-Murnane group in tabletop soft x-ray sources have dramatically expanded the photon energy range over which bright femtosecond-to-attosecond high harmonic (HHG) beams can be generated. Using tabletop mid-infrared (IR) femtosecond lasers, bright soft x-ray supercontinua can be generated that span from the VUV to the keV regions of the spectrum (to below 8 Å), with sufficient flux for applications. Moreover, high harmonic soft x-ray pulses are unique because they are perfectly synchronized to the driving laser, with $\approx \mu\text{W}$ average powers required for advanced chemical spectroscopies.

FY 2014 HIGHLIGHTS

Photoelectron spectroscopy and charge transfer dynamics of isolated quantum dots [1]:

In 2013 work, we reported the first studies of isolated quantum dots. In FY 2014, we expanded on this work by studying dye-quantum dot charge transfer, comparing charge transfer rates of free quantum-dot dye systems with those in solution. Our findings support the hypothesis that reorganization energy of nonpolar solvents plays a minimal role in charge transfer. This work has been submitted.

First isolated attosecond soft X-ray pulses [2]:

Until recently, attosecond pulses were confined to the EUV, limiting the range of molecular/materials systems that could be explored. Here, we experimentally demonstrated a remarkable convergence of physics: when mid-IR lasers are used to drive HHG, the conditions for bright phase-matched soft X-ray generation naturally coincide with the generation of isolated attosecond pulses.

First bright soft x-ray harmonics at kHz repetition rates [3]:

We demonstrated bright soft x ray harmonics at kHz repetition rates driven by 1.3 and 2 μm tabletop lasers. This represents a $> \times 1000$ increase in HHG flux beyond other work.

Publications:

1. J. Ellis, K. Schnitzenbaumer, D. Hickstein, M. Beernink, B. Palm, J. Jimenez, G. Dukovic, H. Kapteyn, M. Murnane, W. Xiong, "Revealing solvent effects on charge transfer between quantum dots and surface adsorbates", submitted (2014).
2. M.C. Chen, C. Hernández-García, C. Manusco, B. Galloway, P.C. Huang, F. Dollar, D. Popmintchev, L. Plaja, A. Jaron-Becker, A. Becker, T. Popmintchev, M.M. Murnane, H. C. Kapteyn, 'Generation of Bright Isolated Attosecond Soft X-Ray Pulses Driven by Multi-Cycle Mid-IR Lasers,' PNAS 111 (23) E2361 (2014).
3. C. Ding, W. Xiong, T. Fan, D. D. Hickstein, T. Popmintchev, X. Zhang, M. Walls, M. M. Murnane, and H. C. Kapteyn, 'High flux coherent super-continuum soft X-ray source driven by a single-stage, 10mJ, Ti:sapphire amplifier-pumped OPA,' Optics Express 22(5), 6194-6202 (2014).

Exploiting Non-equilibrium Charge Dynamics in Polyatomic Molecules to Steer Chemical Reactions

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Principal Investigator: Wen Li

Sr. Investigator(s): Raphael Levine; California-Los Angeles, University of
Henry Kapteyn; Colorado, University of

H. Bernhard Schlegel; Wayne State University
Students: 4 Postdoctoral Fellow(s), 6 Graduate(s), 0 Undergraduate(s)
Funding: \$750,000 (2014)

PROGRAM SCOPE

The main objectives of this proposal are to achieve two major research goals of ultrafast science: 1. Creating and probing photo-induced charge migration dynamics of pure electronic origin on the attosecond to few femtoseconds time scales and studying the role of non-equilibrium charge distributions in inducing selectivity of chemical reactions in polyatomic molecules. 2. Achieving mode-selective chemistry in polyatomic molecules using intense ultrashort mid-infrared pulses. For the first goal, coherent electronic wave packets due to the superposition of a few electronic states in molecular cations will be created with strong field photoionization by ultrashort optical pulses and the subsequent charge migration along the molecular backbone will be monitored by various advanced methods including a photoionization probe implemented with intense attosecond pulse trains (APT) coupled with ion-electron coincidence measurements and attosecond transient absorption with high energy attosecond pulses. Because our theoretical models simulate both the pump and the probe steps with minimum approximations, they will provide realistic experimental parameters and are also well suited to extract electronic dynamics from experimental observations. In the transient absorption experiments, the time-resolved spectra reflect the instantaneous electron density with element and site specificity and thus charge migration dynamics will be captured in real time. For the second goal, we have recently shown in models that mode-selective chemistry can be achieved using intense mid-IR laser excitation through charge polarization on the ground electronic state. The study will be carried out in molecular ions to minimize complications from competing strong field ionization. Mid-IR laser pulses at 3-4 μm will be focused to reach strong field intensity to achieve mode-selectivity in aligned polyatomic molecules. Systems of interest include iodobenzene dication and formyl chloride cation.

FY 2014 HIGHLIGHTS

This is a newly funded project. The starting date was Sept. 1, 2014. We provide no highlights at this point.

Time-Resolved Imaging of Molecules by High-Order Harmonics and Ultra Short Rescattering Electrons

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Funding: \$145,000 (2014)

PROGRAM SCOPE

When a molecule is exposed to an intense ultrashort infrared laser pulse, electrons that were ionized earlier may be driven back by the oscillating electric field of the laser to recollide with the parent ion. If the returning electron recombines with the ion, high-order harmonics are generated. If the returning electron is backscattered elastically by the ion, high energy photoelectrons are emitted. In both cases, the emitted radiation or the scattered electrons contain information on the target molecule. Since laser

pulses of duration of a few femtoseconds are readily available, they can be used to probe the dynamics of molecules with femtosecond timescales. In this project, we established how to extract the spectral behavior of the target molecules from the emitted harmonics. From the photoelectron spectra, our method is called laser-induced electron diffraction. The latter allows us to extract the bond lengths and bond angles of molecules. If the molecule under study is first perturbed by a pump laser, another probe laser can be used to extract the dynamics of molecules as they are under transformation. In this respect, short infrared lasers can be used to probe the evolution of molecules with femtoseconds resolution.

FY 2014 HIGHLIGHTS

In this past period, we demonstrated a new method to analyze electron diffraction patterns from which bond lengths are accurately retrieved. We also studied how to increase the fluence of the returning electrons to enhance diffraction images by combining two- or three-color lasers. In collaboration with an experimental group in Spain, we have been able to extract the C-C and C-H bond lengths of acetylene molecules from the photoelectron spectra generated using 3.1 micron lasers.

Probing electron-molecule scattering with HHG: Theory and Experiment

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Sr. Investigator(s):	Erwin Poliakoff; Louisiana State University
Students:	0 Postdoctoral Fellow(s), 3 Graduate(s), 0 Undergraduate(s)
Funding:	\$465,000 (2014-2016)

PROGRAM SCOPE

This project is a combined experimental and theoretical study of high harmonic generation (HHG) in molecular systems. Additionally we are developing accurate quantum mechanical descriptions of such interactions that involve one continuum electron. The HHG process can be modeled within the three-step picture that consists of tunnel ionization of an electron, then electron wave propagation, followed by the recapture of the electron by photorecombination. This last step, photorecombination, is our particular interest since it involves the same transition matrix elements as the corresponding photoionization process that would be obtained by time reversal. The goal is to probe how resonant and non-resonant processes in electron-ion collisions affect the HHG process. Experimentally, we will consider studies of HHG on a series of polyatomic molecules for which we will map out the behavior as a function of power, focal position, and ellipticity. The objective is to explore the structure found in the HHG spectra as a function of harmonic order. By a comparison with computed cross sections we should be able to identify the processes in the electron continuum that lead to the observed features in the HHG spectra. Specific systems that will be studied include, initially, SF₆, SiCl₄, and CF₄ with later investigation being extended to CS₂, CCl₄, and various substituted benzenes. These systems have known resonant features that may lead to corresponding features in the HHG spectra. Theoretically, we will consider how different levels of approximation for computing the photorecombination matrix elements affect the computed HHG spectra. To enhance our ability to compute the needed matrix elements, we will investigate alternative grid based methods for computing the wave functions for the scattered electrons. The goal will be to overcome the limitations of our current numerical methods which are based on the use of rather slowly convergent single-center expansions.

FY 2014 HIGHLIGHTS

We have completed a study of the high-resolution photoelectron spectrum with partial vibrational resolution of a series of pyrimidine-type nucleobases: thymine, uracil and cytosine. Improved resolution allowed us to identify the electronic origins for the outermost valence electronic states. Striking similarities in the spectral features of all three pyrimidine-type nucleobases lead us to conclude that the features in the cytosine photoelectron spectrum are not due to contributions from multiple tautomers but instead are from unresolved vibrational progressions. We have also completed a study of vibrationally resolved photoionization of acrolein. In our experimental and theoretical study of the non-Franck-Condon behavior in acrolein we found evidence of two localized low energy sigma anti-bonding resonances, which interact to form two resonant states. Excitation of these states leads to significant non-Franck-Condon effects in the excitation of C-C vinyl stretch. We have made considerable progress, in collaboration with Profs. Trallero and Lin at the McDonald Laboratory in the study of molecular HHG. Preliminary work on the HHG spectrum SF₆ found noticeable structure in the experimental spectrum. We varied the gas jet position to change the macroscopic propagation and the effective trajectories of the returning electron. The one feature that is consistently present in the experimental data is the minimum in the HHG spectrum at the 17th harmonic. In the theory we have applied the quantitative rescattering (QRS) theory to isolated molecules and considered the ionization of the electrons from the three most weakly bound orbitals, which have ionization potentials that are all within 1.5 eV of each other. We have examined limitations of the current calculations and found that the asymmetric nuclear vibrations and interchannel coupling may be important to understand the observed spectra.

Properties of Actinide Ions from Measurements of Rydberg Ion Fine Structure

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Funding: \$130,000 (2014)

PROGRAM SCOPE

This project determines certain properties of chemically significant Uranium and Thorium ions through measurements of fine structure patterns in high-L Rydberg ions consisting of a single weakly bound electron attached to the actinide ion of interest. The measured properties, such as polarizabilities and permanent moments, control the long-range interactions of the ion with the Rydberg electron or other ligands. The ions selected for initial study in this project, U⁶⁺, U⁵⁺, Th⁴⁺, and Th³⁺, all play significant roles in actinide chemistry, and are all sufficiently complex that a-priori calculations of their properties are suspect until tested. The measurements planned under this project serve the dual purpose of 1) providing data that may be directly useful to actinide chemists and 2) providing benchmark tests of relativistic atomic structure calculations. In addition to the work with U and Th ions, which takes place at the J.R. Macdonald Laboratory at Kansas State University, a parallel program of studies with stable singly-charged ions takes place at Colorado State University. These studies are aimed at clarifying theoretical questions connecting the Rydberg fine structure patterns to the properties of the free ion cores, thus directly supporting the actinide ion studies. In addition, they provide training for students who can later participate directly in the actinide work.

FY 2014 HIGHLIGHTS

We have successfully completed the studies of Rn-like and Fr-like Th ions, but have so far been unable to learn anything about the properties of the isoelectronic U ions. The difficulties are two-fold: very small resolved signals, and large background rates. During the past year, we have shown that both difficulties are traced to the presence of metastable ions in the U beams extracted from the ECR ion source. As a by-product of these studies, we managed to measure the metastable fraction of the U beams, and achieve a substantial reduction in the background rate. However, despite these advances, we have still been unable to extract any useful information about the U ions.

Theory of Atom Collisions and Dynamics

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Funding: \$126,000 (2014)

PROGRAM SCOPE

The transfer of angular momentum in atomic collisions is the subject that we have investigated in the last year of the project. Our investigations find that angular momentum is transferred to both excited and ionized states of targets and projectiles in the collisions of ions and target atoms. The transfer to excited states produces aligned and oriented atomic states. The oriented atomic states are the most important since they have non-zero mean values of the vector angular momentum and are typically understood in semi-classical terms. We find that in quantum terms the most significant transfer of vector angular momentum occurs near the united atom limit where target and projectile interact strongly to deflect the incident projectile. The transferred angular momentum is observed as orientation of excited states. Some of the angular momentum is transferred to ionized states of the target and projectile as the two species separate. We have shown that this angular momentum produces vortices in the velocity fields of the ejected electrons. A search for such vortices has been successfully completed by our experimental collaborators using an improved COLTRIMS apparatus. This confirms that vortices appear in the velocity field of ionized electrons.

FY 2014 HIGHLIGHTS

The highlight of our work has been the experimental discovery of isolated zeros in the spectrum of electrons ejected in the transfer ionization process. Theory confirms that such isolated zeros are indicative of vortices in the velocity field of ejected electrons.

Photoabsorption by Free and Confined Atoms and Ions

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Funding: \$80,000 (2014)

PROGRAM SCOPE

The goals of this research program are: to provide theoretical support to, and collaboration with, various experimental programs that employ latest generation light sources, particularly ALS, APS and LCLS; to further our understanding of the photoabsorption process; and to study the properties (especially photoabsorption) of confined atoms and ions. Specifically, calculations are performed using and upgrading state-of-the-art theoretical methodologies to help understand the physics of the experimental results; to suggest future experimental investigations; and seek out new phenomenology, especially in the realm of confined systems. The primary areas of programmatic focus are: nondipole and relativistic effects in photoionization; photoabsorption of inner and outer shells of atoms and atomic ions (positive and negative); dynamical properties of atoms endohedrally confined in buckyballs, primarily C₆₀; studies of time delay on the attosecond scale in photoionization of free and confined atomic systems. Flexibility is maintained to respond to opportunities.

FY 2014 HIGHLIGHTS

Confinement resonances, oscillations that occur in the photoionization cross section of an endohedral atom owing to the interference of the photoelectron wave function for direct emission with those scattered from the surrounding shell have been predicted in a broad range of cases; recently, their existence has been confirmed experimentally. Further, the photoionization of endohedral atoms within nested fullerenes, has shown that, as a result of the multi-walled confining structures, the confinement resonances become much more complicated. And we have shown that confinement resonances induce resonances in the time-delay of photoelectron emission. Also a Xe atom endohedrally confined in C₆₀ exhibits a new type of atom-fullerene hybrid which arise from the near-degeneracy of inner levels of the confined atom and the confining shell, in contrast to the known overlap-induced hybrid states around the Fermi level of smaller compounds, and are found to occur in confined noble gas, alkali-earth atoms and the Zn series. The photoionization cross sections of these hybrid states exhibit rich structures and are radically different from the cross sections of free atomic or fullerene states. This also occurs in buckyonions, nested fullerenes which suggests the possibility of creating buckyonions with plasmons of specified character, i.e., designer resonances. We have also explored the interatomic Coulomb decay (ICD) phenomenon in confined atoms and found, owing to hybridization between atomic and shell orbitals, that ICD occurs both ways, from atom to shell and shell to atom, and the rates (widths) are often much larger than the ordinary Auger rates. In addition, we have explained the significant structure in free atom subshell photoionization cross sections many keV above their thresholds found experimentally in Ag; the structure is nonresonant and about 50 eV wide. It was found to be induced by interchannel coupling with inner-shell ionization channels near threshold.

Combining High Level *Ab Initio* Calculations with Laser Control of Molecular Dynamics

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

We use intense, shaped, ultrafast laser pulses to follow and control molecular dynamics, and high level *ab initio* calculations to interpret the dynamics and guide the control.

FY 2014 HIGHLIGHTS

(1) Development of a VUV source: A main experimental development in the past year is a UV pump VUV probe apparatus for pump probe measurements of excited state dynamics and a comparison of weak and strong field ionization of excited states. The pump probe apparatus is almost completed and about to be tested.

(2) Velocity Map Imaging measurements of relaxation in excited molecular cations: We ionize the molecules using our strong field IR laser pulses. Ionization can proceed to a range of ionic states. By measuring the photoelectrons in coincidence with the fragment ions produced by ionization, we can determine the ionic state of the molecule immediately after ionization. Then, the velocity map imaging measurement of the fragment ion measured in coincidence with the photoelectron can be used to determine the kinetic energy release in dissociation for the case of ionization to a dissociative cationic state. A signature of relaxation prior to dissociation is the measurement of fragment ions with kinetic energy release equal to the energy difference between the initial ionic state and ground ionic state at the FC point minus the dissociation energy on the ground state.

(3) Ultrafast relaxation in molecular cations: In strong field dissociative ionization techniques several excited ionic states can be created during the ionization step followed by fragmentation, and it is not clear whether the fragments are produced directly in the excited ionic states or if fast relaxation to the ground ionic state occurs first and fragmentation follows. In order to better understand the processes occurring after ionization and interpret the experimental observables, we have theoretically investigated dynamics of excited radical cations. We have applied trajectory surface hopping molecular dynamics and the Multi-Configurational Time-Dependent Hartree approach to study the dynamics of the uracil radical cation as well as cyclohexadiene and hexatriene radical cations.

Electron-Driven Processes in Polyatomic Molecules

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Funding: \$375,000 (2014-2016)

PROGRAM SCOPE

The focus of this project is the development, extension, and application of accurate, scalable computational methods for studying low-energy electron-molecule collisions, with emphasis on larger polyatomic molecules relevant to electron-driven chemistry in biology and materials processing. Because the required calculations are numerically intensive, efficient use of large-scale parallel computers is essential, and the computer codes developed for the project are designed to run both on tightly-coupled parallel supercomputers and on workstation clusters.

FY 2014 HIGHLIGHTS

We developed computational procedures necessary to explore angle-resolved dissociative electron attachment processes while continuing to explore electron scattering processes in biologically relevant molecules. In collaboration with the Belkacem group (Lawrence Berkeley National Laboratory), who performed the relevant experimental measurements, we studied angle-resolved dissociative attachment to uracil, the simplest nucleobase and thus a prototype for studying electron-induced damage to DNA and RNA. We computed the quantum-mechanical entrance amplitudes that describe how the probability of attaching an electron during a collision varies depending on the direction from which it approaches the molecule. We find, consistent with the Belkacem group's measurements, that the energetic hydrogen anions formed via attachment of electrons with about 6 electron-volts of kinetic energy most likely result from breaking a specific nitrogen-hydrogen bond. These results were published in *Journal of Physical Chemistry Letters*. For some time we have been interested in electron collisions with alcohols, which are actual or potential biofuels. One fundamental issue that has arisen in our studies is the connection between the angular scattering pattern and the molecular structure. Specifically, in the 6 to 10 electron-volt range of collision energies, straight-chain alcohols tend to show one scattering pattern and branched alcohols a different pattern. To explore this further, we collaborated with the experimental group of M. Khakoo (California State University, Fullerton) and the theoretical group of M. Bettega (Federal University of Parana, Brazil) on a study of alcohols and alkyl amines. We found that the trends identified in the alcohols persist in the straight and branched amines. Our results were published in *Physical Review A*.

Electron/Photon Interactions with Atoms/Ions

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Funding: \$80,000 (2014)

PROGRAM SCOPE

To understand the physical mechanism underlying low-energy electron attachment and trapping and creation of new exotic molecules three interwoven and interrelated subprojects have been investigated. Subproject-1 uses our recent novel Regge-pole methodology to: 1) Explore in the near-threshold energy region through the calculation of the elastic total cross sections (TCSs) possible electron attachment to selected atoms resulting in the formation of weakly bound ground and excited anions as resonances; and 2) Demonstrate that the Os^- anion shows dramatic improvement on the catalysis of H_2O to H_2O_2 over recent results obtained using Au^- and Pd^- anions and in the oxidation of CH_4 to methanol using the Au^- anion without the CO_2 emission. Also, recent fundamental anionic, cationic, and neutral atomic metal predictions utilizing density functional theory calculations validate the recent discovery identifying the interplay between Regge resonances and R-T minima as the fundamental atomic mechanism underlying nanoscale catalysis.

In Subproject-2 the CAM method is also being extended to investigate the energy region between the first and the second atomic excitation thresholds where interchannel coupling was found to split degenerate Regge trajectories.

Subproject-3 evaluates the absolute differential oscillator strengths for the photoabsorption of the Xe atoms encapsulated inside the C₆₀, C₁₈₀ and C₂₄₀ in the energy regions both inside and outside the C₆₀ giant resonance, using the time-dependent density-functional theory (TDDFT). These proposed research projects constitute the intellectual contributions to knowledge of the fundamental underpinnings of AMO science.

FY 2014 HIGHLIGHTS

No FY14 Highlights provided.

Theory and Simulation of Nonlinear X-Ray Spectroscopy of Molecules

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Funding: \$512,000 (2014-2016)

PROGRAM SCOPE

Nonlinear X-ray spectroscopy experiments, which use sequences of coherent broadband X-ray pulses, are made possible by new X-ray free electron laser (XFEL) and high harmonic generation (HHG) sources. These provide a unique window into the motions of electrons and nuclei in molecules and materials. This program is aimed at the design of novel X-ray pulse sequences for probing valence electronic excitations, the development of computational approaches for describing core-excited states, and the application of these techniques to specific molecular systems. Nonlinear spectroscopy techniques widely used in the visible and infrared regimes (e.g. time-resolved photoelectron spectroscopy, time-resolved broadband stimulated Raman, coherent control and frequency combs) are extended to the X-ray regime. Applications are made to energy transfer in metalloporphyrin heterodimers, effects of electronic coherence in nanostructured photovoltaics, charge and energy transfer between different metal centers in mixed-valence complexes, and delocalized carbon core excitations in conjugated hydrocarbons. Signatures of vibrational motions and nonadiabatic dynamics in photo-excited molecules are identified via two-dimensional X-ray correlation spectroscopy of multiple core states, time-, frequency-, and wavevector- resolved X-ray diffraction from single molecules as well as photon coincidence detection of multidimensional attosecond X-ray scattering. Other applications include probing electronic and vibrational dynamics in molecules by time-resolved photoelectron, auger-electron, and x-ray photon scattering spectroscopy and three-dimensional attosecond resonant stimulated x-ray Raman spectroscopy of electronic excitations triggered by core ionization.

FY 2014 HIGHLIGHTS

Multiporphyrin arrays are good candidates for artificial photosynthesis and molecular electronics applications. Understanding the excitation energy transfer (EET) pathways in these systems is of considerable interest. Stimulated X-ray Raman spectroscopy (SXRS) signals of various porphyrin heterodimers with different linkers, bonding structures, and geometries were predicted. The time-domain one and two color SXRS signals show coherent excitonic motions, which can be directly mapped into the excited state doorway wavepacket created by the pump pulse, which probes the EET. SXRS

signals are demonstrated to be very sensitive to the chemical bonding and local geometrical environment, and offer a novel window for photophysical and photochemical processes that could help the design of efficient solar energy devices. The SXRS technique was further extended to study multiple core excitation states of the same element. Carbon K-edge signals was simulated for the furan molecule. We also investigated the influence of vibronic coupling on SXRS signals by using the linear coupling exciton-phonon model and the cumulant expansion. Fine-structure features were obtained and analyzed. The nuclei act as a bath for electronic transitions which accelerates the decay of the time-domain signal. Our previously-developed description of time- and frequency-resolved detection of spontaneous emission was extended to the detection of diffracted X-rays. This extension showed the contribution of inelastic scattering events and provided a way to select them in the diffraction signal. We have shown that in elastic terms, they do not contribute to the diffraction from crystals, and must be taken into account for scattering from single-molecule samples. This work was further extended to multidimensional X-ray diffraction in which several X-ray pulses are scattered from the sample. X-ray photon coincidence detection then probes multipoint correlation functions of the electron charge density.

Nonlinear Materials Spectroscopies Probed By Ultrafast X-Rays

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

In this project, ultrashort electromagnetic pulses in the visible, extreme ultraviolet (EUV), and x-ray spectral ranges are all used in complementary efforts to gain experimental access to elementary material excitations and fundamental condensed matter processes on ultrafast time scales and mesoscopic length scales. Of primary interest are heat transport, whose nondiffusive character at short length scales plays important roles in thermoelectric materials and nanoscale devices, and structural evolution in disordered media, which shows dynamics on wide-ranging time scales that have long eluded first-principles description. Central to these phenomena are acoustic phonons, which mediate both thermal transport and the compressional and shear components of structural relaxation. In addition to direct time-resolved observation of thermal transport, longitudinal, transverse, and surface acoustic wave generation and detection are key elements of our experiments in all spectral ranges. We develop and use a variety of methods to excite and monitor acoustic waves and thermal transport on a wide range of length and time scales. For length scales in the roughly 1-100 micron range and acoustic waves in the MHz to low GHz range, we use crossed optical pulses to form an interference or 'transient grating' pattern, directly generating thermoelastic responses with the grating period. The responses are monitored by diffraction of probe laser light. In order to reach higher acoustic frequencies and to monitor heat transport on submicron length scales, spatially periodic structures are deposited onto substrate surfaces so that optical irradiation produces thermoelastic responses at their nanometer periods. The responses are monitored by diffraction of EUV pulses produced by high harmonic generation. To excite GHz-THz acoustic waves, a thin layer or a superlattice structure is irradiated and the acoustic wave is detected by time-resolved optical reflectivity or interferometry.

FY 2014 HIGHLIGHTS

We generated and probed the shortest wavelength surface acoustic waves (SAW) to date, at 45 nm (frequency ~80 GHz), with corresponding penetration depths of ~10 nm. [1,2] This result is significant for nanoscale materials physics because it makes it possible to selectively probe the mechanical properties of very thin films and interfaces, as well as nanostructures deposited on or embedded within a surface. We characterized the acoustic velocity dispersion of 1D and 2D Ni nanostructures with periods 45 nm – 4 μ m. We conducted photoacoustic measurements spanning the 1 MHz - 100 GHz frequency range and combined the results with those of a collaborating group that conducted dynamic mechanical measurements in the mHz-kHz range to determine the complex elastic modulus over 13 decades of frequency, by many decades the most comprehensive study of viscoelastic dynamics ever performed on a single material. The results showed agreement with scaling predictions of mode-coupling theory of supercooled liquids. Finally, we made significant progress on GHz and even THz acoustic wave generation and detection on several fronts. We measured acoustic attenuation mechanisms for acoustic waves in the 0.5-THz frequency range, a step toward mapping the mean free paths of phonons and thereby determining their contributions to thermal transport. We also generated a frequency comb comprising seven acoustic modes spanning a range from 360 GHz to 2.5 THz, the highest coherent acoustic frequency seen to date.

Electron and Photon Excitation and Dissociation of Molecules

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Funding: \$95,000 (2014)

PROGRAM SCOPE

This program studies how energy is interchanged in electron and photon collisions with molecules leading to excitation and dissociation. Modern *ab initio* techniques, both for the photoionization and electron scattering and the subsequent nuclear dynamics are used to accurately treat these problems. This work addresses vibrational excitation and dissociative attachment following electron impact, and the dynamics following inner shell photoionization. These problems are ones for which a full multi-dimensional treatment of the nuclear dynamics is essential and where non-adiabatic effects are expected to be important.

FY 2014 HIGHLIGHTS

Core-level and some inner-valence level photoionization can lead to double ionization that can populate dissociative dication states. Coincident measurement of photoelectrons and fragment ion momenta allows one to study photoelectron angular distributions in the molecular-frame (MFPAD). We have computed MFPADs for the isomerization of acetylene and ethylene and for carbon 1s core ionization of neutral acetylene. We have substituted hydrogen for fluorine, computing the MFPADs for FCCF and lithium for the hydrogen, studying the LiCCLi MFPAD to see the effect of electronegativity on the distributions. Our previous studies of dissociative electron attachment (DEA) of HCCH showed a barrier to reaction in linear geometry. Bending the molecule allowed coupling between the ground and the

excited state of the anion which lowered the barrier so the reaction could proceed. The calculated cross sections and isotope effects were in good agreement with experiment. Recent experiments have produced ion-momentum imaging of the products of DEA in HCCH. The entrance amplitude for this process was calculated to obtain an attachment probability which was integrated over the angle azimuthal to the recoil axis to produce an observable angular distribution. This coincides with the measured angular distribution if the overall rotation of the molecule is slow compared to dissociation and if the fragments recoil at a given angle in the molecular frame, i.e., if the molecular frame recoil axis R is constant over the Franck-Condon region of the neutral. As expected, since theory predicted significant bending during dissociation, this was not found to be the case. However, if the recoil axis was rotated by a fixed amount before averaging the attachment probability over the azimuthal angle the effect of bending can be included. The results with a bending angle around 27 degrees was found to be in good agreement with the observed experimental fragment angular distribution.

Low-Energy Electron Interactions with Liquid Interfaces and Biological Targets

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Funding: \$145,000 (2014)

PROGRAM SCOPE

The primary objectives of this program are to investigate the fundamental physics and chemistry involved in low-energy (1-250 eV) electron and soft x-ray interactions with complex targets. There is a particular emphasis on understanding correlated electron interactions and energy exchange in the deep valence and shallow core regions of the collision targets. The energy loss channels associated with these types of excitations involve ionization/hole exchange and negative ion resonances. Thus, the energy decay pathways are extremely sensitive to many body interactions and changes in local potentials. Our proposed investigations should help determine the roles of hole exchange via inter-atomic and intermolecular Coulomb decay (ICD) and energy exchange via localized shape and Feshbach resonances in the non-thermal damage of biological interfaces.

FY 2014 HIGHLIGHTS

Low-energy electron induced damage of DNA-We have used a sensitive chemical vapor deposited graphene platform for controlled and enhanced sequence dependent DNA damage studies. The use of p-doped graphene substrates enhances DNA breakage due to phosphate mediated parallel adsorption geometries and direct ballistic electron transfer to phosphate sigma* levels. Graphene adsorbed on Au-thin films also provides enhanced electric fields for Surface Enhanced Raman micro-spectroscopy. The combination of these effects allows direct and fast assessment of ≤ 5 eV electron induced DNA damage as a function of base sequence without separations and amplification steps. We have examined LEE induced damage of nucleotides that have a minor change in the sugar structure. Specifically, we examined the LEE induced damage of deoxyadenosine monophosphate (dAMP) and adenosine monophosphate (rAMP) using the graphene Raman micro-spectroscopy. There is no observable change in the Raman spectra after 1 eV electron irradiation. However, significant damage of dAMP occurs after 2 eV electron bombardment. The situation is not the same for the rAMP. There is limited damage even

at 2 eV. Remarkably, the simple addition of an OH^- group to the 2'-C site dramatically changes the stability of the nucleotide with respect to glycosidic bond cleavage and base damage. This is likely related to the nature of the sugar shape resonances and decay products and the ability of charge to be transferred to the phosphate σ^* levels. Our collaboration at Argonne National Laboratory focused on examining x-ray damage of DNA adsorbed on Au in two different conformations. The first is a thiolated form which binds via an S bond and the other is direct adsorption via the bases. The damage cross section was found to be significantly higher for the thiolated DNA, probably resulting from the LUMO initially being less populated and hence more effective in capturing of low energy secondary electrons.

Structure from Fleeting Illumination of Faint Spinning Objects in Flight

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Funding: \$150,000 (2014)

PROGRAM SCOPE

It is now possible to interrogate molecules and their assemblies “in flight” with intense short pulses of radiation, and record “snapshots” before they are destroyed. We are developing a new generation of powerful algorithms to recover structure and dynamics from such ultra-low-signal random sightings. Combining concepts from differential geometry, general relativity, graph theory, and diffraction physics, these techniques promise to revolutionize our understanding of key processes in biological machines, such as enzymes, and ultrafast breaking of bonds in molecules.

FY 2014 HIGHLIGHTS

We have developed a new generation of algorithms capable of determining the structure and conformations of nanomachines from large noisy ensembles of heterogeneous snapshots, and demonstrated this capability in the context of simulated XFEL diffraction snapshots from discrete conformations, and experimental cryo-electron microscope (cryo-EM) image snapshots for continuous conformational changes.

Control of Molecular Dynamics: Algorithms for Design, Analysis, and Implementation

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Funding: \$135,000 (2014)

PROGRAM SCOPE

The control of quantum dynamics is accomplished by seeking a tailored electromagnetic field to meet a posed objective. A search for an optimal control, both in simulation and in the laboratory, occurs over a landscape, which is the physical observable as a function of the control. The topology and general features of these landscapes are important for assessing the ease of identifying optimal controls, the robustness to field noise, and other properties. Optimizing the pulse shape corresponds to climbing the landscape in the control function space. The direct nature of these optimal control trajectories can be quantified by the metric R , defined as the ratio of the length of the control trajectory to the Euclidean distance between its end points. An important, practical assumption underlying landscape analysis is free access to all necessary control resources (i.e., unconstrained laser fields). In practice, constraints will always be present and a basic concern is the control performance achieved upon working with increasingly limited resources. The landscape principles have a universal character and should apply to complex situations including molecular fragmentation, molecular isomerization, ion-atom collisional charge exchange reaction, open quantum systems, and nonlinear many-body dynamical problems involving, for example, ultra-cold Bose-Einstein condensates, etc. One of the main stumbling blocks, both in simulations and in complex laboratory scenarios, is the lack of efficient algorithms to identify optimal control fields. Although the control landscape concepts were developed as a basis to understand quantum control principles, there are emerging practical consequences of this knowledge. A broad variety of research topics was pursued in the general area of controlling quantum dynamics phenomena. The research is theoretical and computational in nature, aiming at developing a deeper understanding of quantum control to extend the laboratory control capabilities.

FY 2014 HIGHLIGHTS

Exploring the impact of resource constraints: We laid out the mathematical foundation for developing practical algorithms to assess the impact of control constraints. Control principles in the chemical sciences: We examined control principles for different families of molecules, all related through various moieties bonded to a common scaffold, utilizing NMR and IR spectral data as the properties of interest. Control landscapes for molecular fragmentation: We examined the landscape principles for laser-driven molecular fragmentation, enabling a series of experimental studies of the landscapes for molecular dissociative ionization of halo-methane molecules. Invariance of quantum optimal control fields to experimental parameters: We utilized landscape principles to demonstrate that an optimal field at one temperature will remain optimal at other temperatures in the laboratory. Control of charge transfer in ion-atom collisions and isomerization: We showed that charge transfer between $H^+ + D$ collisions and ozone isomerization process can be significantly manipulated by shaped pulses. Control landscapes for nonlinear quantum systems: We extended the analysis of control landscape topology to nonlinear quantum dynamics, including the Gross-Pitaevskii equation. Minimal time population transfer for two-level systems by two bounded controls: We analyzed the minimum time population transfer problem for a two level quantum system driven by two external fields with bounded amplitude. Selectively addressing optically nonlinear nanocrystals by polarization-shaped ultrafast lasers: We theoretically studied second-harmonic generation and sum-frequency generation signals produced by nanocrystals driven with broad-bandwidth laser pulses. Exploring quantum control landscape structure: We investigated whether there is a relationship between the control mechanism and the complexity of the trajectory taken through the control space reflected in the value of R .

Atoms and Ions Interacting with Particles and Fields

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PROGRAM SCOPE

This theory project focuses on the time evolution of systems subjected to either coherent or incoherent interactions represented by fields and particles, respectively. This study is divided into three categories: (1) coherent evolution of highly excited quantum states, (2) incoherent evolution of highly excited quantum states, and (3) the interplay between ultra-cold plasmas and Rydberg atoms. Some of the techniques we developed have been used to study collision processes in ions, atoms and molecules. In particular, we have used these techniques to study the correlation between two (or more) continuum electrons and electron impact ionization of small molecules.

FY 2014 HIGHLIGHTS

(1) We modified our time dependent Schrodinger equation programs to perform calculations of attosecond laser-atom interactions for laser intensities where interesting two- and three-photon effects become relevant. (2) We were involved in an experimental/computational project to image a part of the wave function inside an atom. (3) We performed classical calculations of one of the iconic effects of Rydberg atoms in electric fields to study classical-quantum correspondence. (4) We were involved in an experimental/theoretical study of how atoms can have resonance states in extremely strong microwave fields. (5) We performed calculations to investigate the way that many simultaneously excited atoms can exchange energy and ionize. (6) We performed calculations of single and double photoionization of Ne⁸⁺ by direct solution of the time-dependent Dirac equation. (7) We performed calculations of elastic and inelastic scattering of neutral molecules and cold ions in a magnetic field.

Generation of Bright Soft X-Ray Laser Beams

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Sr. Investigator(s):
Students: 1 Postdoctoral Fellow(s), 2 Graduate(s), 1 Undergraduate(s)
Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

This research addresses the challenge of the efficient generation of bright x-ray laser beams. The widespread interest in the use of high intensity soft x-ray and x-ray light that has motivated the commissioning of free electron lasers also inspires the development of more compact and more readily accessible sources of intense soft x-ray laser light for applications. Table-top experiments are conducted at Colorado State University to study the fundamental aspects of the dynamic of soft x-ray plasma

amplifiers and advance the development of gain-saturated, high repetition rate, table-top plasma lasers towards shorter wavelengths. X-ray pump–x-ray probe measurement of the non-linear response of atomic soft x-ray laser plasma amplifiers perturbed by a strong ultrashort soft x-ray pulse are conducted in combination with model simulations to study the ultrafast gain. The linewidth of atomic soft x-ray lasers an important parameter that determines the gain, the saturation behavior, and the shortest pulse width that can be obtained, is measured using a new interferometric single-shot technique. In table-top experiments we extended gain-saturated table-top lasers down to $\lambda=8.8$ nm, and demonstrated 100 Hz repetition rate soft x-ray laser operation generating a record average power of 0.15 mW at $\lambda=18.9$ nm. Experiments in collaboration were also conducted at LCLS to demonstrated strong stimulated x-ray Raman scattering by resonantly exciting a dense gas target with high-intensity femtosecond x-ray free-electron laser pulses.

FY 2014 HIGHLIGHTS

We completed the first x-ray pump–x-ray probe measurement of the non-linear response of an atomic soft x-ray laser plasma amplifier perturbed by a strong ultrashort soft x-ray pulse. A sequence of two time-delayed spatially-overlapping high harmonic (HH) pulses was seeded into an 18.9 nm wavelength nickel-like Mo plasma amplifier to measure the rapid regeneration of the population inversion that follows the gain depletion caused by the amplification of a strong seed pulse. Although such gain recovery time is one of the most fundamental parameters for soft x-ray lasers, it had never been measured. The measured fast gain recovery time of ~ 1.75 ps supports the possibility to generate ultra-intense fully phase-coherent soft x-ray laser by chirped-pulse-amplification in plasma amplifiers. This first x-ray pump- x-ray probe experiment in a soft x-ray plasma amplifier not only uncovers the gain recovery dynamics due to electron collisions but also serves as a diagnostic of the ionization mechanisms in the hot dense plasma with a resolution for a few hundred fs. The results were published in Nature Photonics (8, 381, 2014). In a separate experiment the linewidth of a $\lambda=14.7$ nm Ni-like Pd soft x-ray laser was measured in a single shot using a soft x-ray diffraction grating interferometer that uses the time delay introduced by the gratings across the beam to measure the temporal coherence. The linewidth of atomic soft x-ray lasers is an important parameter that determines the gain, the saturation behavior, and the shortest pulse width that can be obtained. The spectral linewidth of the $4d^1S_0-4p^1P_1$ Ni-like Pd lasing line was measured to be $\Delta\lambda/\lambda=3\times 10^{-5}$ from the Fourier transform of the fringe visibility. This new single shot linewidth measurement technique can contribute to the development femtosecond plasma-based soft x-ray lasers.

Spatial Frequency X-Ray Heterodyne Imaging of Micro and Nano Structured Materials and Their Time-Resolved Dynamics

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Funding: \$420,000 (2014-2016)

PROGRAM SCOPE

Materials are organized in hierarchical structures. Atoms combine to molecules, molecules and atoms combine to nano-scale structures, which, in turn are often embedded in microscopic media. The time

scales of processes vary accordingly from femto and picoseconds for the chemical dynamics of molecules, to hundreds of picoseconds for the transformations of nanoparticles. The goal of this research program is the study of the complex interplay between processes at their varying length and time scales. The kinetics of nanometer-sized materials is studied using Spatial Frequency Heterodyne Imaging (SFHI) an imaging modality that is specifically sensitive to the nano-structure of samples. Ultrafast dynamics of the solvation environment for molecules is studied with picosecond x-ray absorption fine structure (XAFS) spectroscopy using a streak-camera endstation that we developed in collaboration with Bernhard Adams at 7ID-C of the Advanced Photon Source, Argonne National Laboratory. The SFH-imaging studies on the nanoscale focus on the phase transitions of water in nano-confinement. Water in confined spaces can show unusual properties that are not observed in the bulk. For instance, Carbon Nanotubes (CNTs) are made of hydrophobic graphene sheets. Despite the hydrophobic nature of the grapheme sheets, experimental studies have revealed that water can be confined in CNTs. We observe the phase transitions of water and its removal from the external surfaces and inner cavities of CNTs as a function of temperature and time. Ultrafast studies on solvated anions in aqueous solution are studied with picosecond temporal resolution. The goal is not to study the detailed atomic motions of the solutes but rather to study the response of the solvation shells to sudden changes of the solute charge.

FY 2014 HIGHLIGHTS

We used SFHI to observe the removal of water from the outer and inner surfaces of CNTs, establishing the modality's ability to probe nanoscale systems in an aqueous environment over a relatively large temperature range. The capacity for observing macroscopic systems with SFHI was highlighted in this study by imaging multiple macroscopic samples within a single image. The results of this study suggest the potential of SFHI for *in situ* observation of nano-chemical reactions, and possible use of CNTs as high pressure nano-scale reaction vessels. The continuation of this projects aims at measuring the internal pressure of water inside of CNTs. This pressure has been calculated but never measured. Simulations show that a temperatures well-below the water boiling point the pressure inside the CNTs reaches the 0.1GPa regime. The picosecond response of $[\text{Fe}(\text{CN})_6]^{4-}$ and MnO^{4-} in aqueous solution after 266 nm photo excitation has been measured by picosecond XAFS. The results for both complexes show coherent oscillations of the x-ray absorption cross section with a period of approximately 33ps. Coherent molecular motions that modulate the XAFS signal after excitation are conceivable. However, one expects such motions to be on the much faster time-scale of the normal modes of the excited molecule and its immediate solvation shell. On the other hand, classic microwave spectroscopy of water shows a strong absorption band around 30 GHz which has been attributed to librational motions of networks of water molecules. Such motions modulate the dielectric constant of the medium, which in turn modulates the energies of high-lying molecular orbitals of the excited solute. The XAFS oscillations we observe here are the consequence of such dielectric constant modulations in the immediate vicinity of the solute molecule. Thus, to our knowledge for the first time, we observe the concerted motions of the first few solvation shells after excitation of a solute.

Time Resolved High Harmonic Spectroscopy: A Coherently Enhanced Profile of Charge Migration

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Sr. Investigator(s):

Students: 1 Postdoctoral Fellow(s), 3 Graduate(s), 0 Undergraduate(s)

Funding: \$674,999 (2014)

PROGRAM SCOPE

This project is a collaboration between Louisiana State University (LSU), The Ohio State University (OSU) and the University of Virginia (UVa) that intends to meet the challenge of measuring electron dynamics down to the attosecond time scale by initiating and following ultrafast charge migration in a series of carefully chosen molecules. The collaboration aims at establishing a focused theory and computational program at Louisiana State University to guide experiments at OSU and UVa focused on exploring ultrafast electron dynamics in molecules. Individual members of the team have substantial experience in theory and experiment related to high-harmonic and attosecond pulse generation and characterization, including coherent macroscopic propagation, and advanced quantum chemistry methods. The effort will rely heavily on theory to guide the development and interpretation of experiments that will probe dynamics in complex systems, where intuition developed with simpler systems may fail. The measurements will be performed with apparatus currently available (or readily adaptable) at the University of Virginia and The Ohio State University. To encourage cross-fertilization between theory and experiment and, accordingly, to enhance productivity of the collaboration, we will create an active visitors program at each site. We anticipate that students, postdocs, and faculty from the principal (theory) hub at LSU, and the (experiment) nodes at OSU and UVa will spend time at the other sites, with experimentalists visiting LSU during preliminary planning for experiments and post-measurement analysis, and theorists at the laboratories during experimental runs.

FY 2014 HIGHLIGHTS

This grant was funded August 1st, 2014 and so is only few months old at this point. Our first priority has been to find qualified researchers to fill out the roster of approximately 4 postdoctoral and 4 graduate student positions spread over the three institutions. This is very challenging, especially at the post-doc level and beginning late in the calendar year. At present one postdoc has been hired in physics at LSU, with a start date of March 2015. Another in Chemistry at LSU is to be interviewed shortly. Two graduate students are funded at LSU, and the three LSU PIs and these students meet weekly. At OSU a graduate student has begun work on the grant, and one student is to be employed at UVa beginning in the Spring. Both OSU and UVa have active postdoc searches underway. Our second priority has been to organize the collaboration kickoff meeting at LSU. This meeting is scheduled for March 1-3, 2015 and will be hosted at the Center for Computational Technologies (CCT) at LSU. In addition to the six PIs, several postdocs and graduate students, we will also have several outside speakers to provide additional perspectives. Confirmed speakers are Robert Lucchese, Lenz Cederbaum, Catarina Vozzi, Bridgette Cooper, Pascal Salaries, and Erwin Poliakoff. All of the outside speakers are actively involved in high harmonic spectroscopy. Research highlights include the adaptation of the NWChem code to treat strong field ionization, undertaken by Ken Lopata and his student. Mette Gaarde and her student have written a first generation classical trajectory code to evaluate strong field trajectories in elliptically polarized fields. Taken together, these are the first two 'steps' in the three step model which we will use for the theoretical description of high harmonic spectroscopy with an eye towards defining a first set of experiments to be carried at OSU.

Transient Absorption and Reshaping of Ultrafast Radiation

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Funding: \$140,000 (2014)

PROGRAM SCOPE

Our program is centered around the theoretical study of transient absorption of ultrafast extreme ultraviolet (XUV) radiation by atoms and materials interacting with a precisely synchronized near-to-mid infrared (IR) laser pulse. Transient absorption spectroscopy can in principle provide high spectral resolution and high (attosecond) time resolution simultaneously, by spectrally resolving the light transmitted through a sample as a function of delay between the dressing laser pulse and the broadband attosecond XUV probe. As in all transient absorption calculations/measurements, one of the main challenges we confront is the extraction of time-dependent dynamics from delay-dependent information. In addition, we must also account for the reshaping of the broadband XUV light in the macroscopic medium. We study attosecond transient absorption (ATA) using a versatile theoretical treatment that takes account of both the strong laser-atom interaction at the atomic level via the time-dependent Schrodinger equation (TDSE), as well as propagation of the emitted radiation in the non-linear medium via the Maxwell wave equation (MWE), in the single-active electron (SAE) approximation up to now. We are also extending our SAE treatment in atoms to fully-active two electron calculations in helium, in both full and reduced dimensions. These tools allow us to treat the interaction of ultrafast radiation with laser-field dressed atoms down to the single cycle limit with sub-cycle time resolution. Our first principles approach allows us to make close contact with experiment, both explaining existing experiments and identifying fruitful areas for future experiments.

FY 2014 HIGHLIGHTS

We have explored a variety of issues in ATA. Four of these projects were in collaboration with experimental groups, (i) Leone and Neumark, UC Berkeley, (ii) Gallmann and Keller, ETH, Zurich, (iii) Sansone and Nisoli, Politecnico di Milan, and (iv) Sandhu, U. Arizona. (i) "Attosecond transient absorption probing of electronic superpositions of bound states in neon: detection of quantum beats", Beck *et al.*, New J. Phys. 16, 113016 (2014). This study finds that the transient absorption spectra of an IR-laser-dressed neon gas excited by a broadband XUV pulse exhibit oscillations with IR-XUV delay characteristic of superpositions between pairs of spin-orbit split states. (ii) "Multiphoton transitions for delay-zero calibrations in attosecond spectroscopy", Herrmann *et al.*, NJP (2015). We propose a new method for calibrating delay-zero between an IR and an attosecond XUV pulse to within 1 fs, something which has not previously been achieved. (iii) "Polarization control of absorption of virtual dressed states in helium", Reduzzi *et al.*, submitted to PRA (2014). This study explores the dependence of XUV absorption on the relative polarizations of the XUV field and a dressing IR field, and finds that in particular the light-induced features in the ATA spectrum are very sensitive to the relative polarization. (iv) "Beyond the single-atom response in absorption lineshapes: Probing a dense, laser-dressed helium gas with attosecond pulse trains", Liao *et al.*, submitted to PRL (2014). This work explores the interplay between different effects that can change the absorption line shape in an ATA experiment: a microscopic effect due to an IR-induced phase on the time-dependent dipole moment, and a macroscopic effect due to resonant pulse propagation. (v) Postdoc X. Guan has developed an ab-initio two-electron TDSE solver and is exploring ATA in He. This work (in prep. for PRA) focuses on the (surprisingly many) light-induced states which can be seen in the absorption spectrogram.

Strong Field Coherent Dynamics and Control. From Alignment to High Harmonic Generation in Complex Systems

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

Our BES-supported research can be broadly categorized into two conceptually and practically related topics: (1) the design and control of complex material system with strong field concepts, including alignment, 3D alignment, torsional alignment and molecular focusing; and (2) the physics, implications, and potential applications of high harmonics generated from aligned molecules. Whereas the first topic is a generalization of the thrust of our original application, the second has been motivated by the intense interest of the Atomic, Molecular and Optical Science (AMOS) Program in attosecond science and rescattering electrons physics, and has been carried out in collaboration with AMOS experimentalists colleagues. Laser alignment is an approach to control over the spatial properties of molecules wherein a moderately intense laser field excites a broad superposition of rotational levels through sequential Rabi-type cycles, in each of which another one or two units of angular momentum is exchanged between the molecule and the field. In the limit of rigid, isolated diatomic molecules, this approach matured, during the past 15 years from a theoretical dream into a large field of theoretical and experimental research with a growing range of applications in optics and physics. The goal of our research has been to extend the alignment concept from the domain of physics and optics to make a tool in solution chemistry, material research and possibly biology and engineering. High harmonic generation is an approach to producing high frequency radiation through the interaction of atoms or molecules with an intense IR laser pulse. Combined with laser alignment, this method provides a view of the orbitals of molecules. Our research developed a theoretical approach that takes into account both the rotational and the electronic motions of molecules and applied the theory in collaborative work with two AMOS experimental groups.

FY 2014 HIGHLIGHTS

Our work during the past year within the first of the above two components includes two theory development projects and two collaborative research projects with different experimental laboratories. Specifically, we studied: 1. dissipation and rotational quasi-revivals in asymmetric-top molecules - joint theoretical and experimental work with AMOS colleagues; 2. strong field multiple ionization as a route to electron dynamics in a van der Waals cluster - joint theoretical and experimental work with international collaborators; 3. the use of pulling to influence the optical controllability of molecular junctions - theory and computation; and 4. the dissipative dynamics of laser-induced torsional coherences - numerical research. Within the second part of our BES-supported research during the past year, we combined joint research with several AMOS colleagues with a theory of rotational wavepacket imaging via high harmonic generation. In particular we explored: 5. the axis-dependence of molecular high harmonic emission in three dimensions - joint theoretical and experimental work with AMOS colleagues; 6. ultrafast elliptical dichroism in high-order harmonics as a probe of molecular structure and electron dynamics - joint theoretical and experimental work with a second group of AMOS colleagues;

and 7. the application of high harmonic spectra as a rotational wave packet imaging - theoretical research.

Inelastic X-ray Scattering Under Extreme and Transitional Conditions

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Funding: \$150,000 (2014)

PROGRAM SCOPE

The goal of this program is to expand the scope and scientific potential of time-resolved inelastic x-ray scattering (IXS) and closely related x-ray techniques. First, we are using x-ray spectroscopies, soon to include resonant inelastic x-ray scattering, to gain new insight into the energy transfer mechanisms of lanthanide-based phosphors and related luminescent materials and to study the time dynamics of the electronic and structural changes at metal-insulator transitions. Second, we are performing combined theoretical and experimental work to critically test, and substantially improve, the use of IXS methods in the study of dense plasmas, such as in the transitional, 'warm dense matter' regime. Third, we are continuing several collaborations based on IXS instrumentation and methods developed by the PI, including studies of the time-dynamics of energy transfer in photosynthetic proteins and of the f-electron physics of lanthanide elements and compounds at high pressures. Finally, our side-project for laboratory-based XAFS and XES is showing high promise for impact in DOE mission-driven research on electrical energy storage, catalysis, and actinide materials. This new generation of lab-based advanced x-ray spectrometers serves as an important complement and supplement to the DOE synchrotron light sources.

FY 2014 HIGHLIGHTS

FY2014 has seen three major accomplishments under this award: (1) In October 2013 we commissioned a new type of inexpensive lab-based spectrometer for high-resolution x-ray studies, including x-ray absorption fine structure (XAFS) and x-ray emission spectroscopy (XES). We now regularly achieve data that is in perfect agreement with synchrotron-based results. (Seidler, *et al.*, <http://dx.doi.org/10.1063/1.4901599>) The startling performance of this modest instrument has garnered significant interest and has immediately led to the construction at the UW of a mid-scale lab XAFS user facility that emphasizes long-baseline studies of electrical energy storage that cannot, due to the long experimental duration, be frequently performed at synchrotron beamlines. (2) The recent LD67 campaign at LCLS/MEC was led by the PI. While this beam run emphasized laser-shock heating of multicomponent targets (supported by a grant from DOE/FES), complementary x-ray heating experiments were also performed as part of the WDM research under the present award. The results are still under analysis, but show interesting effects in the electronic structure of metallic and metal oxide targets. These results have led to new ideas for multicomponent target designs for x-ray heating studies. (Hoidn, *et al.*, in preparation). (3) Finally, lanthanide compounds and coordination complexes are responsible for a wide range of light-gathering and light-emitting applications. Our recent work at the Advanced Photon Source on luminescent lanthanide complexes demonstrates an unexpected but clear expression of the long-lived 4f intrashell photo-excitation in the time-resolved XAFS of the

lanthanide ion. (Pacold, *et al.*, JACS 2014) Our leading explanation requires a surprisingly dynamic coupling between the 4f and 5d orbitals of the lanthanide ion, a hypothesis that could have broad implications for the correct microscopic understanding of energy transfer in several families of phosphors.

Dynamics of Few-Body Atomic Processes

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Funding: \$364,250 (2014-2016)

PROGRAM SCOPE

The goals of this project are to understand, describe, control, and image processes involving energy transfers from intense electromagnetic radiation to matter as well as the time-dependent dynamics of interacting few-body quantum systems. Investigations of current interest are in the areas of strong field (intense laser) physics, attosecond physics, high energy density physics, and multiphoton ionization processes. Nearly all proposed projects require large-scale numerical computations, involving, e.g., the direct solution of the full-dimensional time-dependent or time-independent Schrödinger equation for two-electron (or multi-electron) systems interacting with electromagnetic radiation. In some cases our studies are supportive of and/or have been stimulated by experimental work carried out by other investigators funded by the DOE AMOS physics program. Principal benefits and outcomes of this research are improved understanding of how to control atomic processes with electromagnetic radiation and how to transfer energy optimally from electromagnetic radiation to matter.

FY 2014 HIGHLIGHTS

Four projects were completed in FY 2014: (1) By solving the two-electron time-dependent Schrödinger equation (TDSE), we studied carrier-envelope-phase (CEP) effects on ionization plus excitation of He to He⁺ (n=2) states by a few-cycle attosecond pulse. The asymmetries in the photoelectron angular distributions with excitation of He⁺(2s) or He⁺(2p) have opposite signs and are two orders of magnitude larger than for ionization without excitation. Thus attosecond pulse CEP effects are significantly amplified in correlated two-electron ionization processes. (2) The CEP dependence of electron angular distributions in double ionization of He by a few-cycle, intense XUV pulse was formulated using perturbation theory in the pulse amplitude. Owing to the broad pulse bandwidth, interference of first and second order perturbation amplitudes produces asymmetric angular distributions sensitive to the CEP. Our perturbation theory parametrization agrees with two-electron TDSE results. (3) The Be harmonic generation spectrum was investigated by solving the two-electron TDSE in an intense laser field. As the laser frequency ωL varies from 1.7 to 1.8 eV, the 7th harmonic becomes resonant sequentially with transitions between the ground state and two doubly-excited autoionizing states. At each resonant frequency, the HHG power spectrum increases by an order of magnitude over a range of harmonics that form a plateau, extending up to the 25th harmonic. (4) Resonance-like enhancements of generalized three-photon cross sections for XUV ionization of Ar, Kr, and Xe were demonstrated using a central-potential model. The resonant-like behavior originates from potential barriers experienced by intermediate- and final-state photoelectron wave packets corresponding to absorption of one, two, or

three photons. Such potential barrier effects are general features of multiphoton ionization processes in most atoms with occupied p- and d-subshells.

Femtosecond and Attosecond Laser-Pulse Energy Transformation and Concentration in Nanostructured Systems

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Funding: \$300,003 (2014-2016)

PROGRAM SCOPE

The program is aimed at theoretical investigations of a wide range of phenomena induced by ultrafast laser-light excitation of nanostructured or nanosize systems, in particular, metal/semiconductor/dielectric nano-structured composites (metamaterials) and nano-clusters. Among the primary phenomena are processes of energy transformation, generation, transfer, and localization on the nanoscale and coherent control of such phenomena. Ultrafast processes in superstrong laser fields in nanostructures recently have received major research attention.

FY 2014 HIGHLIGHTS

During the current grant period of 2013-2014, the following articles with this DOE support have been published [1-7]. The major results are highlighted below:

1.1 Attosecond Control of Dielectrics

[5] We have established the feasibility of manipulating the electronic structure and electric polarizability of a dielectric reversibly with the electric field of light. The established ultrafast reversibility of the effects implies that the physical properties of a dielectric can be controlled with the electric field of light, offering the potential for petahertz-bandwidth signal manipulation.

1.2 Metal Nanofilm in Strong Ultrafast Optical Fields

[1] We have predicted that a metal nanofilm subjected to an ultrashort (near-single oscillation) optical pulse of a high field amplitude $\sim 3 \text{ V/\AA}$ at normal incidence undergoes an ultrafast (at subcycle times $\sim 1 \text{ fs}$) transition to a state resembling semimetal. 1.3 Hot-Electron Nanoscopy Using Adiabatic Compression of Surface Plasmons

[3] We have shown that adiabatic nanofocusing of surface plasmons on a Schottky diode-terminated tip of nanoscale dimensions allows for a plasmon-to-hot-electron conversion efficiency of $\sim 30\%$.

[1] V. Apalkov, and M. I. Stockman, Phys. Rev. B 88, 245438 (2013).

[2] V. Apalkov, and M. I. Stockman, Phys. Rev. B 88, 245438 (2013).

[3] A. Giugni *et al.*, Nat. Nano 8, 845 (2013).

[4] D. Li, and M. I. Stockman, Phys. Rev. Lett. 110, 106803 (2013).

[5] M. Schultze *et al.*, Nature 493, 75 (2013).

[6] H. K. Kelardeh, V. Apalkov, and M. I. Stockman, arXiv:1401.5786 [cond-mat.mes-hall], 1 (2014).

[7] M. I. Stockman, in Plasmonics: Theory and Applications, edited by T. V. Shahbazyan, and M. I. Stockman (Springer, Dordrecht, Heidelberg, New York, London, 2013), pp. 1.

X-rays with Femtosecond Duration and Angstrom Wavelength from a Laser Synchrotron

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Funding: \$150,000 (2014)

PROGRAM SCOPE

X-ray synchrotrons and x-ray free-electron lasers have proven to be transformational technologies for physical and biological sciences. As part of this project, we developed a new type of x-ray source, one which—by virtue of its unique characteristics—may have similar transformational potential. Not only does its x-ray peak brightness and photon energy rival that of 3rd generation x-ray synchrotrons, but its femtosecond x-ray pulse duration is comparable to x-ray free-electron lasers. Moreover, the device is small enough to fit in a university laboratory. The new light source is based on inverse Compton back-scattering, driven by two intense light pulses, each of which are amplified by a single high-power laser system. One laser pulse rapidly accelerates electrons (~ 3 GeV/cm) by means of the laser-wakefield mechanism; and the other laser pulse Thomson-backscatters from the relativistic electrons. The scattered light Doppler upshifts relativistically to high photon energy. The new source has advantages for x-ray science in general, and for the study of ultrafast phenomena in particular. Its exceptionally large x-ray-energy tuning range facilitates probing of almost any element's inner-shell atomic structure. Its femtosecond x-ray pulse duration, coupled to high photon energy, enables ultrafast time-resolved studies with atomic-scale spatial and temporal resolutions. Its synchronization with ultra-high-intensity laser light pulses ($\leq 10^{22}$ W/cm², $a_0 \sim 100$) can merge ultrafast science with high field science; for example, ultrafast dynamics of either highly stripped atoms or extreme states of matter can be investigated. Several of our near-term project objectives include: (i) reduction of the x-ray spectral width, (ii) measurement of the x-ray pulse duration (inferred to be < 10 fs), and (iii) demonstration of an x-ray pump-probe capability.

FY 2014 HIGHLIGHTS

Several novel and unique features of a compact laser-driven Thomson x-ray source were demonstrated at the University of Nebraska, Lincoln [Powers *et al* (2014)]. These include: quasi-monoenergetic spectral width (energy spread $\sim 40\%$), large energy-tuning range (50 keV $\leq E \leq 10$ MeV), and small angular divergence (10-mrad). This is the first demonstration of an all-laser-driven x-ray source with a synchrotron spectrum. It is also a demonstration of the widest tuning range of x-ray source of any type. These attributes, coupled with femtosecond x-ray pulse duration make the source ideal for ultrafast AMO x-ray science. Two other improvements to the x-ray source were also recently implemented. First, the phase distortions of both laser beams used in the system were corrected by means of a novel dual pulse-compressor laser design. This allowed independent control and optimization of the separate laser pulses used to drive the electron accelerator and Thomson scattering [Liu *et al* (2014b)]. Second, a frequency-doubling crystal was used in the scattering beam-line to convert the incident 800-nm light to 400 nm. Doubling the scattering-pulse photon energy reduces the electron energy required to produce x-rays of given energy.

Cold and Ultracold Polar Molecules-Dipolar Collisions and Anisotropic Quantum Gas

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Funding: \$135,000 (2014)

PROGRAM SCOPE

Following the demonstration of a two-dimensional magneto-optical trap for molecular YO, we have been working on the implementation of a three-dimensional MOT. Collaborating with John Doyle's group in Harvard, we have prepared a slow YO molecule beam with a center velocity of 70 m/s from a dual stage buffer gas cooled laser ablation source. We have successfully demonstrated the slowing and cooling of this molecular beam to 20 m/s, and are working now to further cool this beam for loading into a 3D MOT. We expect to achieve this result soon. Evaporation of the hydroxyl radical (OH) remains an exciting prospect for further cooling of chemically interesting molecules and increasing their phase space density. Thus far evaporation efficiency has been limited by collision rate and vacuum lifetime, prompting an investigation of possible improvements. We have designed a new permanent magnetic trap with a factor of 2 steeper gradient and a more favorable loading geometry. Using this trap, we show an order of magnitude increase in the initial density and in collision rate of OH molecules. We are currently working on a detailed investigation of the inelastic and elastic collisions of OH free radicals.

FY 2014 HIGHLIGHTS

On the front of dipolar molecules in the quantum regime, we have recently realized a lattice spin model. By encoding spin in rotational states, we have observed spin exchanges of ultracold polar KRb molecules that are confined in a deep three-dimensional optical lattice. The interactions manifest as a density dependent decay of the spin coherence of the system. In addition to decaying, the spin contrast oscillates, with frequency components that are consistent with the dipolar interaction energies. We have studied these spin exchanges for two different pairs of rotational states, which differ by a factor of two in interaction strength, and find the decay and oscillations to be roughly twice as fast in the case of stronger interactions. A theory comparison based on a cluster expansion agrees quantitatively with our data. These observations were made in a regime where the lattice filling is quite dilute. Our current experimental efforts are focused on increasing the filling fraction. Higher lattice fillings will enable the study of richer physics, such as transport of excitations in an out of equilibrium long-range interacting system. While we have used dipolar interactions of polar molecules pinned in a three-dimensional optical lattice to realize the spin exchange model, the absence of an external electric field precludes the study of the full spin-1/2 Hamiltonian that includes the Ising interaction. Moreover, advanced manipulation of dipolar properties of a bulk molecular gas is also strongly desired. In the near future we will commission the second generation of our KRb polar molecule apparatus that allows large electric fields with the flexibility to apply gradients of the field in arbitrary directions. The same electrodes that supply large DC electric fields also provide AC fields for driving rotational transitions to encode spin.

DOE National Laboratories

Atomic, Molecular and Optical Sciences at LBNL

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Daniel Haxton; Lawrence Berkeley National Laboratory
Students: 2 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding: \$1,441,000 (2014)

PROGRAM SCOPE

The AMOS program at LBNL is aimed at understanding the structure and dynamics of atoms and molecules using photons and electrons as probes. The experimental and theoretical efforts are strongly linked and are designed to work together to break new ground and provide basic knowledge that is central to the programmatic goals of the Department of Energy as formulated in the “Grand Challenges”. The current emphasis of the program is in three major areas with important connections and overlap: inner-shell photo-ionization and multiple-ionization of atoms and small molecules; low-energy electron impact and dissociative electron attachment of molecules; and time-resolved studies of atomic processes using a combination of femtosecond x-rays and femtosecond laser pulses. This latter part of the program is folded in the overall research program in the Ultrafast X-ray Science Laboratory (UXSL). The experimental component at the Advanced Light Source makes use of the Cold Target Recoil Ion Momentum Spectrometer (COLTRIMS) to advance the description of the final states and mechanisms of the production of these final states in collisions among photons, electrons and molecules. Parallel to this experimental effort, the theory component of the program focuses on the development of new methods for solving multiple photo-ionization of atoms and molecules. This dual approach is key to break new ground and provide a new understanding of how electronic energy channels into nuclear motion and chemical energy in polyatomic molecules as well as unravel unambiguously electron correlation effects in multi-electron processes.

FY 2014 HIGHLIGHTS

Applying our COLTRIMS scheme at the ALS to nitrogen and carbon monoxide dimers we could experimentally verify for the first time how energy between molecules can be transferred (10x) more efficiently (resonantly) on an atomic level and ultrafast time scale in a theoretically predicted so-called Resonant Auger Inter Coulombic decay (RA-ICD). We performed experimental measurements and theoretical calculations for the photoionization of CH₄ at the carbon K-edge. The measurements performed with our COLTRIMS method at the ALS combined with the complex Kohn variational calculations of the photoelectron in the molecular frame demonstrated the surprising result that the low energy photoelectrons (~4eV), when averaged over all photon polarization directions, effectively image the geometry of the molecule. We have since found that the situation with molecules containing more than one central heavy atom can be more complicated, with multiple scattering effects leading to additional structure in the MFPADs. The origin of these imaging effects is still not well understood. For

example, we have found that carbon 1s ionization from CF₄ produces an MFPAD that actually anti-images the molecule, that is, the electron is preferentially ejected in directions between the CF bonds, producing a six-lobed octahedral figure. The fundamental importance in electron-driven chemistry provides an impetus for understanding the mechanism of DEA. Our earlier studies of DEA to water, CO₂ and methanol have shown that the topology of the transient anion surfaces relevant to DEA can be quite complicated, with conical intersections between shape resonances, Feshbach resonances and virtual states that can play a role in the dissociation dynamics. We have found that with polyatomic targets, studies of the total dissociation cross sections can belie the complexity of the dissociation dynamics, which is only revealed in angular distribution of the product anions.

Ultrafast Chemical Sciences

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Markus Guehr; SLAC National Accelerator Laboratory
Students: 8 Postdoctoral Fellow(s), 8 Graduate(s), 0 Undergraduate(s)
Funding: \$3,758,000 (2014)

PROGRAM SCOPE

The Ultrafast Chemical Science program has a particular emphasis on ultrafast chemical physics research at SLAC that is enabled by LCLS, the world's first hard x-ray free-electron laser, which began operations at SLAC in 2009. There are three major themes in this program: (1) Imaging on the nanoscale. X-ray imaging using LCLS allows structure determination. (2) Light conversion chemistry. We are particularly interested in the process of photocatalysis within coordination complexes and similar materials. (3) The eV scale in time, space, and field strength. This is the fundamental scale that determines structure and dynamics of electrons in molecules, and motivates advances in sub-femtosecond time-resolution and Angstrom spatial resolution in theory and experiments.

FY 2014 HIGHLIGHTS

The Ultrafast Chemical Science Program made significant progress, with highlights in each of its subtasks during FY 2014. In Attosecond Science, our discovery that multiple electron orbitals can contribute to high harmonics is now used to investigate electronic structural symmetries and sub-femtosecond dynamics in molecules. In our task on non-periodic imaging, we focused on high-speed optical imaging, sample preparation and low-flow electrokinetic microjets for sample delivery. We are developing fluid mixing techniques for time-resolved chemical and biological studies, and development of our electrokinetic microjet resulted in a version that will be used as a standard technique in crystal screening at the Coherent X-Ray Imaging endstation and for future experiments at the LCLS. High-speed imaging schemes developed in our lab will be implemented at the LCLS as well. In strong-field science, we have probed electron delays in above threshold ionization, extending our capability of velocity map imaging in ions to electrons combined with interference techniques, so we can view the quantum evolution of electrons in strong fields with resolution of ten attoseconds or better during strong field ionization. In

solution phase chemistry, key results included using hard x-ray fluorescence to demonstrate that spin crossover in photoexcited Fe compounds occurs stepwise through a triplet intermediate, and using hard x-ray fluorescence to demonstrate that Fe complex spin crossover can be manipulated by ligand and solvent modifications, and anisotropic hard x-ray scattering to study photo-induced bond isomerization. In our nonlinear x-ray optics activity, we published the first paper on phase-matched x-ray frequency doubling and have compared high-harmonic generation in solids and gas phase argon. And in ultrafast theory, we have implemented methods to compute Auger spectra as a probe for excited state dynamics.

EARLY CAREER: Ultrafast X-Ray Studies of Intramolecular and Interfacial Charge Migration

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Students: 1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding: \$500,000 (2014)

PROGRAM SCOPE

Key intramolecular and interfacial charge-transport mechanisms in novel molecular devices for sustainable energy solutions will be studied on their natural timescales and with atomic specificity by means of a new class of ultrafast x-ray experiments. The central motivation is to derive an accurate description not only of the complex electronic structure that emerges from extended molecular and interfacial assemblies, but in particular of the dramatic changes in these electronic structures that, by definition, have to occur in order to enable, for example, long-range charge transfer and/or catalytic function. The combination of different x-ray techniques will provide the capability to test molecular level models of intramolecular and interfacial charge migration by a new set of molecular level probes. Charge migration in porphyrin dyads after photoexcitation will be probed with atomic accuracy by a transient change in atom-specific inner shell photoemission spectra. The arrival of charge carriers on dye-sensitized semiconductor surfaces will be timed with femtosecond precision by the transient change of Auger cascades. Electronic dynamics at bulk-heterojunction interfaces will be observed from different sides of the interface by time-resolved near-edge coherent diffractive imaging experiments. Laboratory based experiments in LBNL's Ultrafast X-ray Science Laboratory (UXSL) will be combined with studies at 4th generation light sources such as the Linac Coherent Light Source (LCLS) and complementary measurements at 3rd generation synchrotrons such as the Advanced Light Source (ALS).

FY 2014 HIGHLIGHTS

In a concerted effort of femtosecond time-resolved x-ray photoelectron spectroscopy (TRXPS) performed at the Linac Coherent Light Source (LCLS) and constrained density functional theory (CDFT) calculations, an interfacial charge-transfer state has been identified as the intermediate electronic configuration that precedes free charge carrier generation upon photoexcitation of a film of ZnO nanocrystals sensitized with N₃ dye molecules. The results provide an important benchmark for the long-standing quest to identify the fundamental mechanisms underlying the performance differences of TiO₂ and ZnO-based hybrid molecule-semiconductor systems for photo-induced charge generation. The LCLS based femtosecond time-resolved experiments have been complemented by picosecond time-resolved experiments at the Advanced Light Source (ALS). A novel TRXPS technique has been developed that provides an electron bunch-length limited temporal resolution of ~70 ps (FWHM) and that can be

applied in all operating modes of the ALS (2-bunch and multi-bunch) while making use of a large fraction of the total ALS X-ray flux. The new capability has been employed to characterize the transient surface photovoltage (SPV) response of a nanoporous, N₃-sensitized ZnO semiconductor substrate due to photoinduced interfacial charge-injection and recombination dynamics. The measurements demonstrate a substantial SPV response of the sintered nanocrystal film and provide direct insight into the dynamics induced in the electron acceptor of the dye-semiconductor interface. The development of a new *in operando* picosecond time-resolved x-ray absorption spectroscopy (TRXAS) technique has been initiated at the ALS to study interfacial electron dynamics in photoelectrochemical devices under application-like conditions. Preliminary *in operando* TRXAS spectra have been recorded for a photoelectrochemical cell based on a thin film hematite (α -Fe₂O₃) working electrode exposed to an aqueous NaOH electrolyte.

EARLY CAREER: Strongly-Driven Attosecond Electron-Dynamics in Periodic Media

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Funding: \$500,000 (2014)

PROGRAM SCOPE

Fundamental strong-field response in crystalline solids involves attosecond electron dynamics. High-density and periodicity of the solid-state make these dynamics markedly different from those in the gas phase. Observation of non-perturbative high-order harmonics in bulk crystals subjected to strong mid-infrared laser fields has been attributed to these sub-cycle electron dynamics. Unlike in a gas, the solid-state exhibits many body problems making these dynamics very rich, and consequently the mechanism for high-order harmonic generation in high-density periodic system is of current debate. The scope of this program is to initiate, control and measure attosecond electron dynamics in periodic media by using strong, waveform controlled mid-infrared laser pulses. This research will advance our understanding of fundamental high-intensity laser interactions in transparent solids particularly focusing on the fundamental differences to the gas phase attosecond AMO.

FY 2014 HIGHLIGHTS

This program began in August 2014. We are setting up a high-intensity, mid-infrared laser system and an experimental chamber for measuring temporal characteristics of high-order harmonics in crystals. In this setup, we will be able to measure the phase of individual harmonics with respect to the laser phase, so called atto-chirp. In analogy to the gas phase attosecond AMO, these time-domain measurements test the suitability of solid-state harmonics for the synthesis of attosecond pulses.

EARLY CAREER: Understanding Photochemistry using Extreme Ultraviolet and Soft X-Ray Time Resolved Spectroscopy

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Principal Investigator: Markus Guehr

Sr. Investigator(s):

Students: 4 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)

Funding: \$502,000 (2014)

PROGRAM SCOPE

The scientific scope of this early career program is a better understanding of photochemistry using ultrafast spectroscopy with high photon energies. Reactions driven by sunlight power nearly all biological functions and are thus responsible for most of the energy resources available on earth. The key question in the matter-light interaction is about the conversion of light energy into other forms of energy. Some molecules transform a large fraction of the light energy into changes in chemical bonds or into a charge transfer. Others distribute the photon energy over many vibrational modes leading to heating without bond change. This selectivity and the efficiency of the light induced processes in matter is the great question in light-matter interaction.

To obtain a better understanding of the light-energy conversion, we combine optical femtosecond photoexcitation with extreme ultraviolet (EUV) and soft x-ray (SXR) femtosecond pulses that serve to probe the molecular dynamics related to nuclear-, electronic- or spin-relaxation. This spectral range provides two crucial advantages. First, the high photon energy probe pulses accomplish to monitor the full molecular relaxation via the emission of photoelectrons. This is in contrast to optical probes that generally accomplish only the photoemission from un- or weakly relaxed molecules. Second, the EUV and SXR pulses provide element and site specificity due to the spectrally distinct absorption and emission features of core electrons. In the EUV domain, we are able to observe the 3d-3p resonance features of 3d transition metals. In the SXR domain, the carbon, nitrogen and oxygen K edges are of particular importance for our work. We use laboratory based femtosecond high harmonic generation (HHG) sources in the range of 20-100 eV; synchrotrons with a wide spectral range from the EUV to the high SXR and the Linac Coherent Light Source (LCLS) providing high pulse energy femtosecond pulses in the soft and hard x-ray range.

FY 2014 HIGHLIGHTS

During this past year we fully commissioned and performed first experiments with our extreme ultraviolet photoelectron/photoion spectrometer. We use pulses of 14 eV photon energy to probe the dynamics on photoexcited molecular states via photoelectron and photoion spectroscopy. We compared the transient photoelectron spectra with multiphoton ion-spectra of perylene after UV excitation of the S_1 state. We found a stark discrepancy in the two different transient signals reflecting the same molecular dynamics. The EUV probe directly leads from the S_1 to the cationic states; the multiphoton probe process involves several neutral resonant states in between the S_1 and cationic states, as we know from signal vs. IR intensity measurements. These intermediate states play a crucial role in shaping the observed transient. Our study shows systematically that intermediate resonances in multiphoton transitions can enhance the sensitivity to molecular dynamics but at the same time are also much more difficult to interpret.

Furthermore, we studied the optically induced insulator-to-metal transition (IMT) of a VO_2 film with EUV diffraction in the range of the vanadium 3p-3d resonance (M-edge). The sample was excited by two optical pulses creating an excitation grating. Performing the experiment above and below the critical temperature for the IMT allowed to separate the effect of the IMT from the acoustic response of the

sample. The IMT creates an ultrafast increase in the diffraction near the vanadium M-edge at very short times.

EARLY CAREER: the Multiconfiguration Time-dependent Hartree Fock (MCTDHF) Method for Interactions of Molecules with Strong Ultrafast High-energy Laser Pulses

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Funding: \$500,000 (2014)

PROGRAM SCOPE

Recent advances in laser technology have made accessible a range of experiments involving short laser pulses. Using such pulses we can excite molecules in various ways and then watch how the energy flows within the molecule, in real time. Doing so permits us to understand and design systems like quantum computers and photosynthetic complexes. We would like to be able to calculate what will happen in a given experiment; theoretical results are always important for designing experiments and explaining the results. However, it is difficult to calculate what happens to a molecule exposed to an arbitrary laser pulse and there are no established methods to do so, even with a supercomputer. Recently the Multiconfiguration Time-Dependent Hartree-Fock (MCTDHF) method has been shown to be viable for this purpose. To be the most useful tool, the method must be able to calculate the dynamics of larger molecules, including the effects of nuclear motion. The goals of this research problem are to apply the MCTDHF method to small systems (atoms and diatomic molecules) that are currently being studied, and to develop the additional capabilities needed to apply the method to larger systems.

FY 2014 HIGHLIGHTS

The program consists of three interlocking thrusts: code development, method development and applications. We made major progress in all areas. Most of the effort in 2014 was spent on code development. We compiled separately the software for three coordinate systems; others may easily be added. We are implementing nonadiabatic rotational motion and improving the treatment of nonadiabatic vibrational dynamics, for diatomics. Methods development was enabled by synergy with the SciDAC project, and the polyatomic capability is now implemented for fixed nuclei without exterior complex scaling. We are calculating valence absorption cross sections for methane. Also in this area, it is necessary to go beyond full configuration interaction. In the publication accepted 12/23/2014 to Phys Rev A, 'Two methods for restricted configuration spaces within the MCTDHF method,' we completed the derivation of MCTDHF for arbitrary configuration spaces. Many authors have published papers on the subject, all with specialized treatments. We derived the general equations for arbitrary spaces, showing that most treatments fall within the simplest category. In the applications area, our primary focus is on wave mixing. We applied Domcke's method to transient absorption of Helium and O₂. The next step in transient absorption experiments is to move to a perpendicular geometry and use several identical XUV pulses in a fan arrangement. We calculate the corresponding signals to make a prediction for the generalization of Chen, Bell, Neumark, Leone *et al*, PRA 86, 063408. I have implemented nonphysical, complex-valued, 'rotating' wave pulses. Issues of gauge invariance notwithstanding, it is clear that the method accomplishes a decomposition of the signal that can be used to chart the paths through which

energy flows in molecules. Preliminary results will be submitted for publication in early 2015. A paper on stimulated Raman in NO, submitted 9/17/2013, was published 11/21/2014.

Engineered Electronic and Magnetic Interactions in Nanocrystals

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Funding: \$776,000 (2014)

PROGRAM SCOPE

Chemically synthesized semiconductor nanocrystals (NCs) have been extensively studied as both a test bed for exploring the physics of strong quantum confinement as well as a highly flexible materials platform for the realization of a new generation of solution-processed optical, electronic and optoelectronic devices. Due to readily size-tunable emission, colloidal NCs are especially attractive for applications in light-emitting diode (LED) displays, solid-state lighting, lasing, and single-photon sources. It is universally recognized that the realization of these and other prospective applications of NCs requires a detailed understanding of carrier-carrier interactions in these structures, as they have a strong effect on both recombination dynamics of charge carriers and spectral properties of emitted light. A unifying theme of this project is fundamental physics of electronic and magnetic interactions involving strongly confined carriers/spins with focus on control of these interactions via size/shape manipulation, doping/heterostructuring, and “interface engineering.” Our goals in this project include: the development of high-efficiency NC-based LEDs free from detrimental effects of Auger recombination such as efficiency “roll-off” at high currents; realization of electrically pumped single-NC light sources; the achievement of NC lasing under continuous-wave excitation; and demonstration of ferromagnetic behavior in optically-active NCs doped with magnetic impurities.

FY 2014 HIGHLIGHTS

- Clear demonstration of the effect of Auger recombination (AR) on the performance of quantum dot (QD) light-emitting diodes (LEDs). [Nature Commun. 4, 2661, 2013; featured as DOE/BES highlight, May 2014] When LEDs are fabricated from alloyed core/shell QDs with suppressed AR, we observe a ca. two-fold improvement in the absolute external quantum efficiency, and a marked reduction in efficiency “droop” at high currents, compared to devices made with conventional core/shell QDs.
- Development of a new type of “dot-in-bulk” nanostructure for dual-color light emission. [Nano Lett. 14, 486, 2014] Heterostructures comprising a quantum-confined CdSe core and an ultra-thick (>25 monolayers) CdS shell separated by a thin interfacial barrier emit two-color light under both optical and electrical excitation with effective emission color that is tunable by excitation photon intensity or applied bias voltage.
- Single-QD spectroscopy produces new insights into the influence of the core/shell interface potential on the suppression of AR. [Nano Lett. 14, 396, 2014; ACS Nano 8, 7288-7296, 2014] Through time-resolved time-tagged single QD spectroscopy, we observe that while having essentially no effect on single-exciton decay, the interfacial alloy layer in a core/alloy/shell QD

heterostructure leads to a systematic increase in biexciton lifetimes, and biexciton emission efficiency as inferred from two-photon correlation measurements.

- Development of time-resolved spectro-electrochemistry for probing and controlling recombination processes in complex QDs. [Nano Lett. 14, 3855, 2014] A novel experimental apparatus allowed us to study the time resolved emission of QDs under an electrochemical bias. The result is unprecedented insight into the influence of charge-trapping processes QDs, and a means for activation and tuning of core- and shell-emission channels, including the tuning of the effective emission color from red to green in light-emitting devices based on dot-in-bulk QDs.

Ultrafast X-Ray Science Laboratory (UXSL)

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Students: 11 Postdoctoral Fellow(s), 5 Graduate(s), 0 Undergraduate(s)
Funding: \$2,057,000 (2014)

PROGRAM SCOPE

The Ultrafast X-ray Science Laboratory (UXSL) exploits the use of short X-ray and XUV pulses to provide basic knowledge of ultrafast dynamics of photo-excited atoms and molecules from the natural time scale of electron motion to the time scale of the chemical transformations. There are five subtasks in the UXSL effort, reflecting the essential strategy of attacking these problems using an approach that applies an entire arsenal of ultrafast experimental and theoretical methodology spanning time scales from attoseconds to picoseconds to the study of systems that include atoms and molecules in the gas phase, clusters, nanodroplets and condensed phase transition-metal complexes. The set of experimental and theoretical projects that constitute the Ultrafast X-ray Science Laboratory are an integrated effort to develop novel applications of emerging ultrafast experimental techniques and to provide basic knowledge that is central to the programmatic goals of BES/DOE.

FY 2014 HIGHLIGHTS

- 1) Made first detection of quantum vortex lattices in rotating helium nanodroplets by X-ray coherent diffractive imaging. Isolated pure and Xe-doped nanodroplets imaged by single X-ray (1.5 keV) pulses at Linac Coherent Light Source. Vortices imaged by doping the droplets with Xe atoms, which are attracted to the vortex cores where they cluster and act as contrast agents for detection of elusive quantum phenomenon.
- 2) Refined and applied transient absorption spectroscopy to observe coherent superposition of Rydberg states below first ionization potential of neon. Attosecond pulse prepares the coherent superposition. Then NIR pulse interrogates initial excitation by perturbing induced polarization at varying time delay.
- 3) New reaction microscope completed and used in experiments on ethylene employing two photon processes generated from pump-probe schemes using femtosecond light pulses at 8 and

14 eV to break the C=C bond. Preferred emission of the CH_2^+ fragments along polarization direction found while fragments from higher-order excitation showed isotropic distribution. Surprising peak at zero kinetic energy release was discovered.

- 4) Completed first time-resolved X-ray absorption near edge spectroscopy and extended X-ray absorption fine structure spectroscopy studies of transient electronic and molecular structure of bimetallic $\text{Mn}_2(\text{CO})_{10}$ following photodissociation. This compound is a prototype for understanding solution photolysis of organometallic compounds with metal-metal bonds.
- 5) Using extensive computer simulations developed a new scheme for measurement of polarization of atoms and molecules above ionization threshold induced by intense IR or visible laser pulses using transient absorption methods. Also completed *ab initio* trajectory studies exploring post-electronic excitation dynamics of small helium clusters as a simulation counterpart to UXSL experiments.

Atomic, Molecular and Optical Physics

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Funding: \$981,000 (2014)

PROGRAM SCOPE

The Argonne AMO physics program conducts experimental and theoretical research on x-ray interactions, inner-shell processes, and applications of x-ray methods at the Advanced Photon Source (APS) storage ring and at the LCLS and SACLA x-ray free-electron laser (XFEL) facilities. The APS is our primary source of intense, tunable, polarized x rays for time-resolved laser-pump/x-ray-probe experiments on the photochemical dynamics of solvated molecules. To exploit the full x-ray flux of the APS, we use high-repetition-rate lasers for pump-probe experiments at megahertz pulse rates. This enables high precision measurements of the electronic and atomic structures of laser-induced transient states. X-ray absorption and core-hole decay produces high charge states on the atomic sites of a molecule and the system Coulomb explodes. We use reaction microscopes to measure the breakup momenta of the fragment ions in coincidence. The APS measurements motivate the research performed at XFELs on the photo-dynamics of solvated molecules and on intense x-ray interactions with gas-phase atoms and molecules. Theory is a key component of the research program by predicting phenomena that motivate experiments and by simulating measured results. Optical lasers can trap, move, and orient nanoparticles and provide a new route towards the assembly of nanomaterials. The AMO program includes a collaboration with Professor Norbert Scherer at the University of Chicago to develop optical tweezers and traps for x-ray diffraction and coherent x-ray imaging of nanoparticles at the APS.

FY 2014 HIGHLIGHTS

By implementing high-repetition-rate lasers at the APS, time-resolved x-ray absorption (XAS) and x-ray emission (XES) spectra of laser-excited molecules in solution are recorded with high precision. The high statistical precision allowed the first observation of valence-to-core x-ray emission in short-lived

transient species. This capability was applied to characterizing transient electronic and atomic structures of:

- Ligand dissociation, ligand substitution, and electron detachment in aqueous ferrocyanide.
- The low-to-high-spin transient state of iron(II)-bis-terpyridine.
- Dynamics of charge carriers and trapping sites in aqueous zinc oxide nanoparticles.

The APS measurements on aqueous ferrocyanide and zinc oxide both motivated experiments in the femtosecond/few-picosecond regime at the SACLA XFEL. Inner-shell photoionization and core-hole decay in gas-phase xenon and xenon difluoride were compared to explore molecular effects. Total cross sections and partial ion yields were measured at the Wisconsin soft x-ray storage ring and compared with relativistic coupled-cluster calculations of the resonant states. These results guided subsequent measurements using two femtosecond x-ray pulses at the LCLS. The first pulse creates an inner-shell hole and the second pulse probes the molecular dynamics. A Monte Carlo rate equation method was developed to simulate the complex ionization dynamics of atoms exposed to an intense XFEL pulse. The calculations were the first to include resonances systematically and thus to identify resonance-enhanced x-ray multiple ionization pathways that play an essential role in ultraefficient production of high charge state ions in Ar, Kr and Xe. The code runs on advanced computational platforms. Future applications are planned on the interactions of intense x rays with molecules, clusters, and nanoparticles.

Catalysis Science

Institutions Receiving Grants

Oxo Rhenium and Molybdenum Catalysts for the C-O Cleavage and Deoxygenation

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Funding: \$165,000 (2014)

PROGRAM SCOPE

Limited supply of nonrenewable crude oil and its impact on climate change necessitate a shift towards renewable resources. Plants are solar factories that utilize carbon dioxide, water, and sunlight to make lignocellulosic matter. However, biomass components, xylans, cellulose, and lignin are rich in oxygen. Therefore, the goal of this project is to develop efficient and selective catalytic processes that remove oxygen atoms from biomass derived compounds.

FY 2014 HIGHLIGHTS

We have shown that vicinal diols can be deoxygenated to alkenes using methyltrioxorhenium (MTO), water and air stable commercial catalyst, under reasonable conditions (140°C) with molecular hydrogen or secondary alcohols as the reductant. We have extended the MTO-catalyzed reaction to biomass derived glycerol and polyols to make alkenes and high value chemicals (HVCs) that can be used as drop in chemicals in polymer synthesis. The kinetics and mechanism of the MTO-catalyzed deoxydehydration (DODH) reaction has been elucidated revealing a previously unrealized rhenium(V)/rhenium(III) cycle. To explore rhenium complexes with various oxidation states and their potential in acceptorless dehydrogenation (AD) reactions, we synthesized and characterized several rhenium dicarbonyl complexes supported by PNN pincer ligation in three different oxidation states, rhenium (I), (II), and (III).

Structure-Reactivity Relationships in Multi-Component Transition Metal Oxide Catalysts

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

Cobalt-containing oxides are active for a wide range of reactions that typically require vastly more expensive Pt-group metals. The catalytic activity, however, is sensitive to the full range of effects seen in heterogeneous catalysis, including particle size dependence, support effects, sensitivity to preparation

conditions, and doping and impurity effects. Even for the binary oxide, the active phase of the material is an open question. Therefore, we have been working on determining how the geometric and chemical structures of Co oxide surfaces influence the catalytic properties of these materials. We use a surface science approach involving atomic resolution scanning probe microscopy coupled with macroscopic spectroscopic and reactivity measurements.

FY 2014 HIGHLIGHTS

We have focused on cobalt oxide clusters on Au. Although the O₂ pressures are orders of magnitude above the Co₃O₄ dissociation pressure, we find only CoO at low oxide coverages. The CoO surface exhibits a moiré pattern due to the lattice mismatch with Au. Interestingly, the moiré maxima, each with 220 atoms, become the building blocks that determine the cluster shape. The minimum number of maxima seen was three; no clusters containing four, six, or eight maxima were detected. The shapes of the stable clusters alternated between trapezoids and regular and elongated hexagons until the size approached 6,000 atoms, after which the clusters consistently displayed the expected asymmetric hexagonal shape due to the different energies of the alternating edges. The results highlight how even weak substrate interactions affect the stability and shape of catalytic clusters. The Co oxide clusters large enough to be oxidized to Co₃O₄ displayed “Y” defects due to CoO oxidation starting only at specific edges; since the Au determines the density of these edges, it plays a key role in determining the oxidation rate of the clusters. The Co₃O₄ could be reduced to CoO by CO, demonstrating that they are active for CO oxidation. We began to monitor the reduction of Co₃O₄ with STM video imaging. At 570 K in vacuum the Co₃O₄ clusters could be imaged; leaking in CO caused continual rapid restructuring of the clusters that made imaging difficult. Thus a phase transition was seen but obtaining atomic scale information will require fine tuning of the temperature and CO flux. To quantify the increased stability of small CO clusters and to characterize CO oxidation under catalytic conditions, Ambient Pressure XPS measurements were performed at Brookhaven National Laboratory. The results showed that the stability of even the large Co₃O₄ clusters was decreased by orders of magnitude compared to the bulk, and that the smaller Co oxide clusters could not be oxidized to Co₃O₄ even at 0.5 Torr O₂.

Modeling Catalyzed Growth of Single-Wall Carbon Nanotubes

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Funding:	\$110,000 (2014)

PROGRAM SCOPE

Single-wall carbon nanotubes have unusual physico-chemical properties that make them promising materials for a variety of electronics, biomedical, micro and nanofluidics, and other innovative applications. Such properties are mainly determined by the tubes diameter and by their degree of helicity, also known as chirality. Single-wall carbon nanotubes may be grown by decomposition of a carbon-containing species over nanocatalyst surfaces using chemical vapor deposition methods. Significant progress has been made in the last decade refining the synthesis process with the goal of obtaining a well-defined product useful for specific applications; however, a big challenge remains in trying to elucidate the reasons behind the chirality selectivity found under specific operation conditions,

nature of the precursor gas, and type of catalyst/support utilized in the synthesis. Thus, a large component of that challenge is associated with the catalytic process. In our previous work we used density functional theory and reactive molecular dynamics to demonstrate the existence of a structural correlation between the nanoparticle and the nascent nanotube at different growth stages. Such correlation can be dominated by either the nanotube (inverse template effect) or the nanoparticle (template effect). Thus achieving chirality control depends on determining synthesis conditions where crucial structural features of the nanoparticles are maintained during growth. The objective of this new work is to elucidate further aspects of the growth mechanism such as the nature of the active species being added to the nanotube rim, the influence of non-reactive gases, the role of surface and bulk carbon diffusion, the role of bimetallic surfaces, and the conditions for horizontal growth. These studies will allow a systematic search of nanotube growth conditions where the nanoparticle stability can be optimized thus allowing template effect and selective growth.

FY 2014 HIGHLIGHTS

A strong interaction between the catalyst surface and the graphitic lattice of the nanotube was found to be necessary for healing and formation of nanotube defects. Defects can be healed independently of their degree of embedment of the defective structure into the tube structure. Diffusion and catalytic events at the catalyst/tube interface are the main sources of nanotube structural recovery on the catalyst surface. Optimal growth conditions are identified that allow significant structural healing in nanotubes. Selective functionalization of low-coordinated surface sites on quartz surfaces cause exposure of low-coordinated Si atoms that bond strongly to nanotube walls. Saturation of low-coordinated oxygen also favors carbon nanotube adhesion to the substrate. A chirality preference was confirmed on functionalized surfaces towards zigzag over armchair nanotubes. Magnetization effects on the surface originated by the presence of adsorbed functional groups were found to enhance adsorption of arm-chair nanotubes compared to that on clean surfaces. Based on the findings, it was suggested that surfaces may be engineered to favor horizontal adsorption of specific chiralities along preferential directions. Analyses of atomic scale movies obtained with an environmental transmission electron microscope (Dr. R. Sharma, NIST) showed how carbon atoms assemble developing a graphene sheet that wraps around a catalyst nanoparticle forming a nanotube. It was found that the catalyst nanoparticles have adjacent surfaces with divergent work of adhesion for graphene. This difference is crucial for nanotube growth efficiency because it offers the required anchoring and lift-off sites. Our results indicate that the faceting geometry of the nanoparticles determines the nanotube cap structure, thus defining both the diameter and the chiral angle of the single-walled carbon nanotubes during their birth.

Chemoselective Oxidations Using Visible-Light Responsive Semiconducting Oxides

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Funding: \$400,000 (2014-2016)

PROGRAM SCOPE

This research program builds on our efforts in using sol-gel chemistry to generate alloyed compositions of solid-state materials that can be used as either direct photocatalysts or as visible light-absorbing

compounds to transfer charge carriers to tethered molecular catalysts. This inorganic chemistry research addresses the Catalysis Science mission of examining the elementary steps in chemical reactions occurring at homogeneous-heterogeneous (molecular/solid) interfaces. Moreover, we have expanded the reaction scope of our work beyond water oxidation (from the previous funding cycle) to include photo(electro)chemical oxidation of alcohols and amines to generate value-added chemicals.

FY 2014 HIGHLIGHTS

In this first year of funding, we have demonstrated that a known iron-based water oxidation catalyst can be modified synthetically to include a phosphonate tethering group that binds the complex to the semiconductor, tungsten oxide (J. Am. Chem. Soc. 2014, 136, 1694). On their own, semiconducting oxides have the drawback that their valence band holes are so oxidizing that the resulting chemical reactions are non-specific. Typically stable anions such as chloride and sulfate used in common electrolytes react faster than does water. The advantage of the tethered architecture is that embedding a molecular catalyst, even at the low loading of 1 nm per square cm, onto tungsten oxide gives rise to a nearly 50% enhancement in the photocurrent density, in the voltammetry, and a 30% increase in the Faradaic efficiency for oxygen evolution from water. This result sets the stage for carrying out other chemoselective oxidation reactions using visible light.

Nanoscale Surface Chemistry and Electrochemistry of Clean and Metal-Covered Faceted Substrates: Structure, Reactivity and Electronic Properties

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

During catalytic reactions the shape (morphology) and size of supported metal nanoparticles can vary and sometimes undergo reversible shape changes in response to variations in the reacting gases, which in turn can induce changes in their reactivity and selectivity. These changes are attributed to the strong interaction between adsorbates (e.g. reactants, intermediates) and metal nanoparticles, which is related to adsorbate-induced morphological evolution (i.e. faceting) of metal surfaces. The goal of this project is to explore new aspects of the relationship between nanoscale metallic features and (electro)chemical reactivity/selectivity. We focus on three research areas: 1) fabrication and characterization of adsorbate-induced nano-faceting of atomically rough metal single crystal surfaces such as hcp (11-21), hcp (12-31) and fcc (210); 2) reactivity and selectivity of the faceted metal surfaces in catalysis; 3) utilization of faceted metal surfaces as nanotemplates for growth of metallic nanoclusters with regular spacings and synthesis of nanostructured metallic monolayer electrocatalysts. The faceted metal surfaces, free of any support material, represent a unique type of nanoscale model catalysts which can bridge the material gap between metal single crystal surfaces and supported metal nanoparticles. The well-defined facets allow for detailed experimental and theoretical characterization that provides insights into structure–reactivity/selectivity relationships, which is crucial for improving reactivity and selectivity by controlling the nanoscale morphology and size distribution of heterogeneous catalysts and electrocatalysis.

FY 2014 HIGHLIGHTS

We have written an invited review article for a book entitled 'Catalysis by Materials with Well-defined Structures' (Elsevier B.V., ISBN: 978-0-12-801217-8, 2015). The detailed studies on N-, C- and O-induced nano-faceting of Re(11-21) have been completed. The surface morphology (e.g. two-sided ridges, three-sided pyramids, four-sided pyramids, etc.) of Re(11-21) can be tailored on the nanometer scale by careful control of adsorbate species (N, C, O), adsorbate coverage and surface temperature. The (2x1) reconstructed Re(11-21) surface acts as a precursor state for N-induced faceting of Re(11-21) (J. Chem. Phys. 2014). When C-induced faceting of Re(11-21) occurs C atoms prefer to bind at four-fold sites of the Re facets (Catal. Lett. 2014). We have found microscopic structural connections between the various morphologies on O-covered faceted Re(11-21), which provide a natural explanation to the pathways of mass transport in reversible morphological transformation on faceted O/Re(11-21) (Surf. Sci. 2015). We have detected formation of N₂O in oxidation of ammonia by co-adsorbed oxygen on clean planar Ir(210) and clean faceted Ir(210), which is the first observation of N₂O production in catalytic ammonia oxidation under UHV conditions (< 1x10⁻⁹ Torr) (Catal. Lett. 2015). The selectivity of the reaction to N₂, N₂O and NO on Ir can be tuned by oxygen pre-coverage, surface morphology and facet size.

Photocatalysis of Modified Transition Metal Oxide Surfaces

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Funding: \$150,000 (2014)

PROGRAM SCOPE

The scope of this project is to establish a cause-effect relationship for structurally and compositionally modified photocatalysts. Gaining molecular scale understanding of how surface and bulk modifications alter the photocatalytic reactivity to aid the design for next generation photocatalysts

FY 2014 HIGHLIGHTS

The prototypical photocatalyst TiO₂ exists in different polymorphs, the most common forms are the anatase- and rutile-crystal structures. Generally, anatase is more active than rutile, but up to now no consensus existed to explain this difference. This year we have demonstrated that it is the bulk transport of excitons to the surface that contributes to the difference. Utilizing high-quality epitaxial TiO₂ films of the two polymorphs we evaluate the photocatalytic activity as a function of TiO₂-film thickness. We found that for anatase the activity increases for films up to ~5 nm thick, while rutile films reach their maximum activity for ~2.5 nm films already. This shows that charge carriers excited deeper in the bulk contribute to surface reactions in anatase than in rutile. Furthermore, we measure surface orientation dependent activity on rutile single crystals. The pronounced orientation-dependent activity can also be correlated to anisotropic bulk charge carrier mobility, suggesting general importance of bulk charge diffusion for explaining photocatalytic anisotropies.

Studies of Metal-Metal Bonded Compounds in Group Transfer Catalysis

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Funding: \$155,000 (2014)

PROGRAM SCOPE

The overall goals of this research are (1) to define the fundamental coordination chemistry underlying successful catalytic transformations promoted by metal-metal bonded compounds, and (2) to explore new chemical transformations that occur at metal-metal bonded sites that could lead to the discovery of new catalytic processes. Transformations of interest include metal-promoted reactions of carbene, nitrene, or nitrido species to yield products with new C–C and C–N bonds, respectively. The most promising suite of transition metal catalysts for these transformations is the set of metal-metal bonded coordination compounds of Ru and Rh of the general formula $M_2(\text{ligand})_4$, where $M = \text{Ru or Rh}$ and ligand = a monoanionic, bridging ligand such as acetate. Development of new catalysts and improvement of catalytic conditions have been stymied by a general lack of knowledge about the nature of highly reactive intermediates in these reactions, the knowledge that is to be supplied by this work. Our three specific objectives for this year have been (A) to trap, isolate, and characterize new reactive intermediates of general relevance to catalysis, (B) to explore the electronic structure and reactivity of these unusual species, and how these two properties are interrelated, and (C) to use our obtained mechanistic knowledge to design new catalysts with a focus on Earth-abundant first-row transition metal compounds.

FY 2014 HIGHLIGHTS

Yao, S. A.; Corcos, A. R.; Infante, I.; Hillard, E. A.; Clérac, R.; Berry, J. F. *J. Am. Chem. Soc.* 2014, 136, 13538-13541. An “Intermediate Spin” Nickel Hydride Complex Stemming from Delocalized $\text{Ni}_2(\mu\text{-H})_2$ Bonding
Kornecki, K. P.; Powers, D. C.; Ritter, T.; Berry, J. F. *Prog. Inorg. Chem.* Vol. 58, Karlin, K. D., ed.; John Wiley & Sons, Inc.: Hoboken, 2014, p. 225-302. Metal-Metal Bonded Compounds as Catalysts for C–H Functionalization

Ammonia and Hydrazine: Transition-Metal-Catalyzed Hydroamination and Metal-Free Catalyzed Functionalization

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Funding: \$155,000 (2014)

PROGRAM SCOPE

Nitrogen-carbon bonds are ubiquitous in products ranging from chemical feedstock to pharmaceuticals. Consequently, the so-called hydroamination reaction, the addition of an N-H bond across a carbon-carbon multiple bond, a process, which ideally occurs with 100% atom economy, has been widely studied. Various catalysts have been found to promote this chemical transformation, although many limitations still remain; one of the most prominent is the use of NH_3 and NH_2NH_2 as the amine partners. In fact, the utilization of ammonia in catalytic olefin hydroamination was listed among the ten greatest challenges for catalytic chemistry over a decade ago, and it remains unsolved today. More broadly speaking, apart from a few heterogeneous processes, examples of transition metal catalyzed functionalization of NH_3 are rare. The importance of these challenges is readily understandable since more than 100 million metric tons of NH_3 are produced per year, and the production of amines is similarly huge. Therefore the goal of this project is the development of novel ligands and types of transition metal complexes, which are efficient for transforming ammonia and hydrazine. In addition, we search for metal-free catalyzed processes for the functionalization of these amines. Indeed, the activation of NH_3 and NH_2NH_2 without transition metal centers offers an alternative paradigm in the continuing search for efficient catalytic systems, and should allow considerable reductions in the cost of important chemical processes.

FY 2014 HIGHLIGHTS

We have developed a novel synthetic route giving access to mesoionic carbene and cyclopropenyliene supported gold chloride complexes, which after chloride abstraction allow for the first transition metal-catalyzed functionalization of both nitrogens of parent hydrazine. We have shown that, similarly to transition metal nitrido complexes involved in the Haber-Bosch hydrogenation of N_2 into NH_3 , the first stable nitrene prepared in our laboratory acts as a nitrogen atom transfer agent. It also allows for the isolation of the first phosphoranimines, and copper- and silver-nitrene complexes, which are important intermediates in phosphazene polymerization, and in aziridination and amination reactions, respectively. Friedel-Crafts reactions typically require Lewis acid catalysts and are therefore generally unsuitable for basic substrates. Classical textbooks especially emphasize their incompatibility with amines, which is a major limitation due to the ubiquity of this organic functionality. We have found that cationic gold complexes, supported by our stable electrophilic carbenes, promote the hydroarylation of styrenes and norbornene, as well as enones, by dialkylanilines. Thanks to the peculiar properties of cyclic (alkyl)(amino)carbenes (CAACs), we have isolated the first complexes featuring gold, copper, cobalt and iron in the zero oxidation state. The stability of these complexes is not only a demonstration that CAACs are very efficient redox active ligands, but it might allow for new types of catalytic cycles. It has already been shown that the iron complex can activate N_2 at -78°C . We also found that CAACs allow for the preparation of mixed-valence gold(I)/gold(0) trinuclear clusters, the smallest members of the $(\text{LnAu}_m)_x^+$ family. Such gold clusters have attracted a great deal of interest due to their potential applications for nanoelectronic devices, medical science, and catalysis

EARLY CAREER: Catalyst Design for Small Molecule Activation of Energy Consequence

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Funding: \$150,000 (2014)

PROGRAM SCOPE

Small molecule substrates can be interconverted as a mechanism for advanced energy storage in conjunction with renewable energy sources. The type of chemistry and catalysis necessary to develop alternative energy sources rely on small molecule (e.g. H₂O, N₂, CO₂) activation processes. Activation of these substrates relies on mediation of multi-electron, multi-proton reaction sequences. Stepwise delivery of these reagents can incur large overpotential costs as high-energy intermediates are encountered, evidenced by the strong chemical oxidants and reductants commonly employed to initiate reactivity in molecular-based catalysts. One possible method to circumvent these high-energy pathways is to mediate concerted multi-electron reaction pathways, bypassing high-energy intermediates altogether. This program seeks to develop a general approach for transforming ubiquitous small molecules (e.g., N₂, CO₂) into viable building blocks for synthetic fuels through the development of a new class of polynuclear catalysts. Our efforts in catalyst development will be described in the following contexts: (1) design ligand platforms to proximally accommodate multiple metal centers; (2) establish the ability of the polynuclear complexes to mediate multi-electron redox transformations, both electrochemically and via small-molecule activation processes; and (3) develop the multi-electron, stoichiometric reactivity discovered into viable catalytic processes to transform small molecule substrates into value-added chemicals (e.g. fuels).

FY 2014 HIGHLIGHTS

(1) Using our synthetic protocols for the assembly of cluster-based materials, we have prepared homotrimeric complexes of each 1st row metal from V to Zn. (2) Mixed-metal clusters are afforded via sub-stoichiometric substitution or metathetical routes from alkaline-earth metal based clusters. (3) Using this strategy we were able to understand the onset of high-spin electronic structure via magnetic metal ion doping. This was achieved by comparing the following clusters: Fe₂, Fe₂Mg, Fe₂Ca, Fe₂Sr, and Fe₃. We investigated this series by magnetometry and uncovered geometrical changes that influence the overall spin-states obtained. (3b) Using redox-neutral metal clusters we are able to stabilize late transition metal ions in unusually high-spin states. For example, a Co₂Zn cluster was able to support CoIV with concomitant capture of an imido linkage. (4) The onset of single molecule magnetism is enhanced via the materials which display a strong preference for direct-exchange magnetic interactions (e.g., direct, intracluster M-M orbital overlap). As a result, high magnetic spin ground states have been observed existing to room temperature (e.g., S = 10 persistent to 300 K). (5a) We have shown that cluster-based main-group aggregates showcase orthogonal chemistry as a function of molecular spin-state. A bridging Co₃(_{m3-N}) complex is classically nucleophilic as a diradical anion, but classically electrophilic as a neutral species. (5b) We have asserted that cluster spin-state is directly proportional to the reactivity of the cluster as a molecular unit. Through isolation of the diamagnetic Ni₃ cluster, we have shown it is remarkably stable against atom and group transfer reagents. Only via reduction to the mono-anion is the Ni₃ platform rendered reactive for nitrene or S-atom capture. Via subsequent oxidation, the Ni₃ cluster has been found to be stable across five discrete oxidation states, far exceeding the typical availability from mononuclear Ni-based molecules.

EARLY CAREER: One-Pot Catalytic Conversion of Biomass and Alkanes: Kinetically Coupling Deoxygenation and Dehydrogenation Pathways

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Funding: \$150,000 (2014)

PROGRAM SCOPE

This research focuses on developing kinetic and mechanistic understanding of heterogeneous catalytic process involved in the hydrodeoxygenation (HDO) of biomass-derived polyfunctional molecules using either CH₄ or molecular H₂ as hydrogen sources on non-precious metal catalyst formulations. The stoichiometric hydrogen deficiency of carbohydrate feedstock implies that all conversion processes must remove oxygen and concurrently increase hydrogen content to form liquid hydrocarbon products. We report that non-precious metal based carbide formulations are selective catalysts for oxygen-removal from lignin and cellulose-derived biomass monomers at atmospheric pressure.

Recent publications:

1. Jeremy Bedard, Do-Young Hong, Aditya Bhan; "CH₄ dehydroaromatization on Mo/H-ZSM-5: 1. Effects of co-processing H₂ and CH₃COOH." *Journal of Catalysis* 306 (2013) 58.
2. Jeremy Bedard, Do-Young Hong, Aditya Bhan; "Co-processing CH₄ and oxygenates on Mo/H-ZSM-5: 2. CH₄/CO₂ and CH₄/HCOOH Mixtures." *Physical Chemistry Chemical Physics* 15 (2013) 12173.
3. Wen-Sheng Lee, Zhenshu Wang, Weiqing Zheng, Dionisios Vlachos, Aditya Bhan; "Vapor phase hydrodeoxygenation of furfural to 2-methylfuran on molybdenum carbide catalysts." *Catalysis Science & Technology* 4 (2014) 2340.
4. Wen-Sheng Lee, Zhenshu Wang, Ryan Wu, Aditya Bhan; "Selective vapor phase hydrodeoxygenation of anisole to benzene on molybdenum carbide catalysts." *Journal of Catalysis* 319 (2014)44.
5. Jeremy W. Bedard, Do-Young Hong, Aditya Bhan; "C to H effective ratio as a descriptor for co-processing light oxygenates and CH₄ on Mo/H-ZSM-5." *RSC Advances* 4 (2014) 49446.

FY 2014 HIGHLIGHTS

We report: (i) Mo₂C is a stable and highly selective catalyst for the low temperature (550 K) vapor-phase HDO of lignin-derived phenolics to form benzene, toluene, and xylene (BTX) - aromatics that are each amongst the 50 most produced chemicals worldwide. Oxygen modification of the surface prevents successive hydrogenation reactions. (ii) Acid site densities on metal carbide surfaces can be reversibly tuned by a factor of ~30 using an O₂ co-feed, which reversibly creates Brønsted acid sites on the carbide surface without altering bulk crystal structure as inferred from titration studies and reaction kinetics of isopropyl alcohol dehydration. The acid and metallic characteristics of carbidic formulations of highly oxophilic metals such as Molybdenum can therefore be systematically tuned by co-processing oxygen. (iii) The carbon-to-hydrogen effective ratio is a single value descriptor of oxygen removal pathways when co-processing C₁-C₃ oxygenates and CH₄ on Mo/ZSM-5 formulations reflecting the stoichiometric loss of oxygen as carbon monoxide when co-processing oxygenates and CH₄ at high temperatures (~950 K).

Single-Molecule Fluorescence Imaging for Studying Organic, Organometallic, and Inorganic Reaction Mechanisms

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

Our laboratory has pioneered direct imaging techniques by fluorescence microscopy to study chemical reaction mechanisms and catalyst efficiencies by determining the location of reactivity with single-molecule and -particle sensitivity and spatial resolution. These studies have established our ability to characterize mechanisms, measure kinetics, and image single reactions at individual metal complexes with organic ligands similar to those used in homogeneous and supported-molecular heterogeneous catalysts in industrial- and research-scale synthesis. Improvement of catalytic reactions relies on accurate knowledge of the phase and structure of the active catalyst. Our program provides knowledge of the phase and partial structural information (with a long-term goal of additional structural information) of the active catalyst through sensitive microscopy techniques that are capable of deconvoluting multistep systems. One focus is the characterization of reactivity distributions of supported molecular catalysts under “normal” synthetic reaction conditions (e.g., ambient pressure and temperature, solution phase, and standard reagent concentrations). Supported molecular catalysts have the advantage of facilitating separations and recyclability and limiting reactor fouling while in theory retaining some of the uniformity of the environment around the active metal center possessed by homogeneous molecular catalysis. In part the difficulty in characterizing these heterogeneous systems arises from the measurement challenge of characterizing the reactivity distributions that are obscured by ensemble averaging in traditional bulk measurements. Our research program removes this ensemble averaging through the development of single-molecule and -particle microscopy technology.

FY 2014 HIGHLIGHTS

We overcame these measurement challenges via optical and SEM microscopy in studies of single resin beads of a commercial supported molecular ruthenium metathesis catalysts during the polymerization of norbornene. The major findings of these studies are: 1) over half of the support beads are fully inactive to the detection limits of the methods and lack active sites that contribute significantly to the generation of the polymer; 2) on the active beads, the majority of polymer forms at only a small number of locations; 3) the ruthenium is more evenly distributed across and within a catalyst bead than is distributed the catalytic reactivity; 4) polymer morphology is influenced by its growth from individual locations; and 5) this microscale, heterogeneous spatial reactivity suggests an untapped potential for substantially increased catalyst efficiency in this commercial system which was previously unrecognized. Tapping into this potential lead to improving the catalytic efficiency of the supported catalyst by deforming the resin support beads prior to the reaction, enabling 90% conversion to polynorbornene in 10 minutes, instead of the original 27% conversion with the unmodified commercial support as received from the manufacturer.

Novel Transport of Porous and Composite Nanostructures

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Abhaya Datye; New Mexico, University of
Students: 1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding: \$180,000 (2014)

PROGRAM SCOPE

This project is based on our unique abilities to synthesize model nanoscale architectures incorporating and interfacing monosized catalytic NPs and NP arrays with ultra-thin nanoporous membranes that are further 'adjustable' by conventional and plasma assisted atomic layer deposition (ALD) methodologies developed by our team in our prior grant cycle. Building on the concept of model nanoparticle catalytic reactors, the overall goal of our work is to fabricate catalytic systems with adjustable particle size, composition, spacing and accessibility along with tailorable NP/support interfaces and steric constraints. Additionally and importantly we have devised synthetic approaches to prepare these model systems in ultra-thin, electron transparent forms allowing direct TEM structural and chemical imaging of the parent system and its morphological and chemical evolution during the course of a realistic catalytic process. Also the 'thinness' of our systems, e.g. membranes or 2D-MoS₂, maximizes the catalytically accessible surface area per gram and guarantees short diffusion distances, minimizing contact times of desired products with active sites and enhancing flux of catalytic membrane reactor systems. A direct immediate goal is to use our model membrane reactors to investigate *in situ* TEM imaging of catalyst structure and chemistry during the oxidative dehydrogenation (ODH) of light alkanes. Based on the combination of ultrathin mesoporous silica membranes modified with ALD, we are also developing strategies for the synthesis of energy-relevant separation membranes with enhanced properties, e.g. CO₂ sequestration, resulting from well-defined chemical and dimensional asymmetry as inspired by natural biological systems and channels. Our research efforts are supported by molecular and atomic-level modeling and imaging of our membrane and catalytic architectures, with the goal of understanding the relationship between nanostructure and functional properties.

FY 2014 HIGHLIGHTS

During the past year, our research has refined the synthesis and characterization of nanoporous silica membranes, fabricated via evaporation-induced self-assembly (EISA) with Pluronic ethylene oxide/propylene oxide/ethylene oxide (PEO/PPO/PEO) triblock polymer templates, demonstrating for the first time truly variable pore size (4.5 to 20 nm) with controlled 3D pore network structure in porous silica films. We have also refined the atomic layer deposition (ALD) process for deposition of conformal vanadium oxide and nanoparticulate PdO and Pt into these silica membranes, and characterized material stability toward coarsening by heat, x-rays, and electron beam. Combining EISA and ALD, we fabricated an initial set of model reactors (Pt nanoparticles within 8 nm silica pores) on TEM transparent silicon nitride membranes (20 nm thick) for characterization of structure and reactivity in the laboratory of Robert Schlögl at the Fritz Haber Institute, Berlin, Germany. Using proton transfer reaction mass spectrometry coupled to a temperature controlled microreactor, we were able to measure catalytic activity in our model reactor architecture, even with a real active area of less than 1 mm², and determined the onset temperature of CO oxidation. On the same sample, we were able to image the Pt

nanoparticle/SiO₂ interface using high resolution TEM, demonstrating the capability of combining reaction measurements with detailed studies of active site morphology before and after catalytic testing. Other work in this year continued our efforts at using ALD modification of silica to create asymmetric biomimetic separation membranes, with the development of a nano-stabilized enzymatic membrane for CO₂ capture with unprecedented flux and selectivity. Finally, we used high resolution TEM to image exfoliated MoS₂ to develop correlations between atomic structure rearrangement and photocatalytic activity of this material during dye-sensitized H₂ evolution.

Supported Metal Nanoparticles: Correlating Catalytic Kinetics, Energetics and Surface Structure

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Funding: \$450,000 (2014-2016)

PROGRAM SCOPE

Most solid catalysts used for industrial chemical reactions that produce fuels and clean up pollution from the generation and use of fuels consist of transition metal nanoparticles dispersed across the surfaces of oxide and carbon supports. These materials also serve as electrocatalysts and photocatalysts for energy conversions. This experimental research program aims to provide the basic understanding needed to develop better catalyst materials for these applications. Well-defined model catalysts consisting of metal nanoparticles supported on single-crystal oxide and carbon surfaces are structurally characterized using surface spectroscopies, and the energies of the metal atoms in these particles, the metal/support adhesion energies (E_{adh}) and the energy of adsorbed intermediates on these particles are measured by calorimetry techniques we developed that are unique in the world. Our prior results proved that these energies depend strongly on the size of the particles and the nature of the support, and that they correlate with their catalytic properties, which correlate with the chemical potential of the metal atoms. This is measured by metal adsorption calorimetry and found to increase strongly with decreasing particle size below 6 nm and, for a given size and metal, with decreasing E_{adh} . We are seeking to develop predictive ability for E_{adh} on many metal/support combinations. This in turn will allow us to predict metal chemical potential versus particle size and support. We also seek to further refine the correlation of this chemical potential with their catalytic properties (chemisorption strengths, elementary-step rates, net catalytic reaction rates and sintering kinetics), and to utilize this to predict better catalyst materials. The energies of adsorbed intermediates are also measured by calorimetry, and their rates are measured by transient kinetics. These energies of metal atoms and adsorbates also serve as benchmarks for improving computational methods.

FY 2014 HIGHLIGHTS

We developed an improved adsorption calorimeter for metal atom adsorption energies on single-crystal surfaces, and applied it to study the energetics of Cu, Ag and/or Au nanoparticles on Fe₃O₄(111) and CeO₂(111). Comparing the resulting adhesion energies for Cu, Ag and Au on CeO₂(111) to our earlier results for many metals on MgO(100) show that E_{adh} for any one metal is larger by ~ 1.7 J/m² on CeO₂(111) than on MgO(100). We also developed the first crude ranking of adhesion energies of different supports to the same metal: MgO(100) \approx TiO₂(110) < Al₂O₃(0001) < CeO₂(111) \leq Fe₃O₄(111).

Metal chemical potential at small size ranks in the reverse. For different metals on the same oxide surface, Each scales with the heat of formation of the oxide of that metal from metal gas plus O₂. Taking advantage of this new understanding of metal / oxide bonding energies and their relationship to sintering rates, we developed a more sinter-resistant Pt catalyst in collaboration with Younan Xia at Georgia Tech. It involves a thin SiO₂ coating which completely surrounds the Pt nanoparticles on the TiO₂ nanofiber support. Xia developed a clever wet-chemical approach to synthesize this that is more applicable in industrial catalysis than alternative approaches that have been used to make similar structures. The average size and number density of supported metal nanoparticles is very important, and these can be estimated by electron microscopies. However, this is very time consuming and often impossible when the particle size is only 1-2 nm. However, electron spectroscopies (XPS and AES) provide quantitative information on both the total amount of adsorbed metal and the particle thickness in this size range. The Hemispherical Cap Model has been widely used to relate their signal intensities to the particles size and number density, but this only works for electron detection normal to the support surface. We derived a new algorithm that extends this model to other detection angles.

Catalytic Upgrading of Key Biorefining Building Blocks to Renewable Chemicals, Polymeric Materials, and Liquid Fuels

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Funding: \$150,000 (2014)

PROGRAM SCOPE

The central objective of this project is to develop efficient, selective, and cost-effective catalytic systems for upgrading of key biorefining building blocks, derived from catalytic conversion of plant biomass, into value-added chemicals, polymeric materials, and liquid fuels. More specifically, the proposed work seeks to accomplish the following three specific objectives: (a) developing cost-effective and recyclable catalysts for selective upgrading of C₅-C₆ biorefining building blocks into C₁₀-C₁₂ intermediates and for integrating biomass conversion and upgrading processes; (b) transforming the upgraded intermediates into polyols, polyurethanes, polyesters, and diesel fuels; and (c) reforming the upgraded intermediates into high-grade C₁₀-C₁₂ liquid hydrocarbon transportation fuels via selective hydrodeoxygenation catalysis. The hypothesis-driven research described in this proposal employs combined experimental techniques for mechanistic, structural, and synthetic studies of catalysis as well as for polymer and nanoscale science. Building upon a key discovery that 5-hydroxymethylfurfural (HMF), an established biorefining building block or biomass platform chemical, can be selectively and quantitatively upgraded into the C₁₂ DHMF (5,5'-di(hydroxymethyl)furoin) in a catalytic and 100% atom-economical fashion, the research proposed for the current grant period will focus on the next-phase of the project: selective upgrading of HMF and two other related C₅ and C₆ biorefining building blocks into higher-energy-density C₁₀ and C₁₂ furoin intermediates and subsequent catalytic reforming of such intermediates into value-added chemicals, polymeric materials, and liquid fuels. The research described in this renewal proposal addresses one of the DOE-BES's priority research directions in Catalysis for Energy, particularly in terms of exploring new catalytic pathways for lignocellulosic biomass conversion and upgrading into chemicals and fuels.

FY 2014 HIGHLIGHTS

We have developed a highly effective new strategy for upgrading biomass furaldehydes to liquid fuels. This strategy consists of organocatalytic self-condensation (umpolung) of biomass furaldehydes into C₁₀–C₁₂ furoin intermediates, followed by hydrogenation, etherification or esterification into oxygenated biodiesel, or hydrodeoxygenation by metal-acid tandem catalysis into premium alkane jet fuels. We have developed an integrated catalytic process for conversion and upgrading of biomass feedstocks into 5,5'-dihydroxymethyl furoin (DHMF), through self-coupling of 5-hydroxymethylfurfural (HMF) via organocatalysis, and subsequently into n-C₁₂H₂₆ alkane fuel via metal-acid tandem catalysis. We have uncovered the role of N-heterocyclic carbenes in glucose conversion into HMF by Cr catalysts in ionic liquids, and introduced organocatalysis into biorefining for biomass conversion and upgrading.

Dedicated Beamline Facilities for Catalytic Research: Synchrotron Catalysis Consortium (SCC)

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Funding: \$369,451 (2014)

PROGRAM SCOPE

Synchrotron spectroscopies offer unique advantages over conventional techniques, including higher detection sensitivity and molecular specificity, faster detection rate, and more in-depth information regarding the structural, electronic and catalytic properties under in-situ reaction conditions. Despite these advantages, synchrotron techniques are often underutilized or unexplored by the catalysis community due to various perceived and real barriers, which will be addressed in the current proposal. Since its establishment in 2005, the Synchrotron Catalysis Consortium (SCC) has coordinated significant efforts to promote the utilization of cutting-edge catalytic research under in-situ conditions. These tasks have been performed by a consortium consisting of PIs and co-PIs from academic, national, and industrial laboratories. The beamlines and facilities are located in the National Synchrotron Light Source at Brookhaven National Laboratory. The PIs and co-PIs have extensive experience in the areas of catalysis, electrocatalysis and synchrotron techniques. The combined expertise of the team members will continue to create the synergy that is necessary to ensure the success of the dedicated beamline facilities for catalytic research.

FY 2014 HIGHLIGHTS

In 2014 we continued to develop integrated characterization tools that are appropriate for carrying out detailed in-situ studies on structure and dynamics of catalysts using synchrotron techniques. We further develop existing experimental methods that have not yet been extensively tested in the limit of real catalytic conditions, on small size particles and with fast acquisition times. We also participated in the transition of the catalysis program from NSLS to NSLS-II. This transition path also includes an intermediate stage by setting up catalysis operations at a dedicated XAS beamline at the SSRL. The SCC team are addressing the following key issues to assist the catalysis community during the transition: (1) coordinating with SSRL by providing personnel, in-situ reactors, and any necessary hardware/software

to accommodate SCC catalysis users during the transition period, (2) creating experimental database, sample preparation protocols, and data analysis methodologies for catalysis research in the new NSLS II beamlines, and (3) planning in-situ measurements of chemical, spatial and temporal properties of working catalysts using the state-of-the-art NSLS II characterization techniques.

Structure-Property Relationship in Metal Carbides and Bimetallic Alloys

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Funding: \$170,000 (2014)

PROGRAM SCOPE

The electronic and catalytic properties of transition metals can be modified by incorporating carbon atoms to form carbides or by alloying with another metal to produce bimetallic alloys. The metal carbides and bimetallic alloys often demonstrate properties that are distinctively different from those of the pure parent metals. The primary goal of the current project is to use selected carbides and bimetallic alloys as model systems to unravel the relationship between the electronic/geometric structures and the chemical/catalytic properties to assist the rational design of catalytic materials. Furthermore, it is becoming apparent of the critical needs to identify alternative catalysts that can either replace Platinum (Pt) or substantially reduce the amount of Pt in many catalytic and electrocatalytic applications. The utilization of metal carbides and bimetallic alloys allows us to explore the possibilities of using these materials to replace or reduce the amount of Pt in catalysis and electrocatalysis.

FY 2014 HIGHLIGHTS

In 2014 we have focused on the utilization of carbide and bimetallic catalysts for the hydrogen evolution reaction (HER) from water electrolysis in two areas: (1) Utilization of monolayer precious metal over carbides in acid electrolyte. Using a combination of density functional theory calculations and experimental measurements we identified a correlation between hydrogen binding energy and HER activity for a wide range of metal-modified carbides with substantial reduction of precious metal loadings. (2) Discovery of non-precious bimetallic catalysts in alkaline environment. The alkaline environment enabled us to design non-precious bimetallic systems for water electrolysis. We have identified several bimetallic catalysts with HER activity similar to Pt, using a combined approach of theoretical and experimental studies on single crystal surfaces, electrochemical evaluation of polycrystalline thin films, and synthesis and test of porous catalysts relevant for device applications.

Chemical Imaging of Single-Particle Photo(electro)catalysis

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Funding: \$170,000 (2014)

PROGRAM SCOPE

The long-term goal of this program is to understand the fundamental principles governing the catalytic, photocatalytic, and photoelectrocatalytic properties of nanoscale catalysts, so as to acquire the knowledge and ability to engineer and control them to achieve desired catalytic properties. To attain this long-term goal, the program has included two major projects studying nanoscale metal and semiconductor catalysts. In one project, we aim to study the chemical catalysis on single metal nanoparticles of various morphologies and probe the catalytic activity and dynamics in a spatiotemporally resolved manner within a single particle. In the other second project, we aim to understand the correlation between surface reactivities of photogenerated holes and/or electrons in a spatially resolved manner on single semiconductor nanostructures under solar water oxidation conditions, as well as the correlation among each nanostructure's hole/electron surface reactivities, photocurrent responses, and structure/morphology. Both projects use super-resolution single-molecule reaction imaging of single particles, which our group has pioneered. The knowledge obtained will help understand the fundamental principles governing the catalytic properties of nanoscale catalysts, contributing to the efforts in meeting society's energy challenge.

FY 2014 HIGHLIGHTS

In FY 2014, we have successfully used super-resolution single-molecule reaction imaging to reveal hidden surface reaction intermediates in single-nanoparticle catalysis (Journal of Physical Chemistry C, 2014, 118, 26902–26911). Detecting and characterizing reaction intermediates is important for elucidating reaction mechanisms, yet challenging because of the low populations of intermediates, especially in heterogeneous catalysis. We studied two complementary types of Au nanocatalysts -- mesoporous-silica-coated Au nanorods and bare pseudospherical Au nanoparticles -- in catalyzing the oxidative deacetylation of amplex red, a synthetically relevant and increasingly important probe reaction. We have revealed a kinetic intermediate, down to the subparticle level. We formulated a quantitative reaction mechanism, which further allowed for the evaluation of the large reactivity inhomogeneity among the individual nanocatalysts. We have also used super-resolution single-molecule reaction imaging, combined with photoelectrochemical measurements of single semiconductor TiO₂ nanorods, to reveal the correlation among surface hole and electron reactivity and local photon-to-water oxidation conversion efficiency (manuscript in preparation). Semiconductor nanostructures are preferred photoelectrode materials for photoelectrochemical water splitting, a potentially economical and sustainable route toward solar energy conversion. At the photoanode, oxygen evolution catalysts (OECs) are generally needed to increase performance. Yet it is unclear what types of surface sites to deposit OEC to achieve optimal performance. We find that surprisingly on TiO₂ nanorods, the reactive sites for water oxidation are also the sites for recombination. This knowledge enables us to deposit site-selectively an OEC to reveal the optimal sites for enhancement in photocurrent and reduction in onset potential, leading to a strategy to rationally engineer photoelectrodes with a minimal amount of catalyst.

Understanding Nitrogen Fixation

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

During the funding period, we have intensively investigated the feasibility of hydrogen atom transfer (HAT) as a means to make new N-H bonds in the coordination sphere of group 4 metallocene complexes. This thrust is motivated by our experience with this class of compounds as well as their rich N₂ functionalization and cleavage chemistry. Our overall goal is to establish design principles which allow for the fixation of N₂ to NH₃ using H₂ as the source of both protons and electrons. In order to develop a catalytically competent system, an understanding of the underlying thermodynamics of HAT to bound nitrogen-containing fragments is key. Towards this end, we synthesized a number of model nitrogen-containing titanium and zirconium metallocene compounds and studied the thermochemistry of HAT as a function of ligand, metal, and hydrogen-atom donor. Initially, we targeted substituted bis(cyclopentadienyl) -titanium and -zirconium amide (NH₂) complexes. In any hypothetical sequence linking N₂ and H₂ to NH₃ via hydrogen atom transfer, the final intermediate is expected to be a metal amide species. Though many metal amides have been reported in the literature, they are known to be unreactive towards H₂ and we were thus particularly interested in the thermodynamics governing the formation of this final N-H bond. By analyzing the pK_a and reduction potentials of a series of group 4 metal amides, we were able to determine the N-H bond dissociation free energies (BDFE) of a variety of complexes and correlate this data to the ligand environment and metal identity. Data for N-H BDFEs in the coordination sphere of a metal is sparse yet essential for designing catalytic systems based on the HAT design principle. With this data in hand, we turned to the investigation of metal co-catalysts capable of catalytically cleaving H₂ and supplying hydrogen-atom equivalents to the nitrogen fragment and demonstrated NH₃ synthesis.

FY 2014 HIGHLIGHTS

Several important milestones were reached during the past year of DOE support. Most notably we have demonstrated the potential of hydrogen atom transfer in the synthesis of ammonia from its elements. Such research is critical if this important molecule is to be synthesized from carbon-neutral and renewable hydrogen. This approach is a new strategy for breaking strong metal-ligand bonds and opens new opportunities for catalysis as a key challenge in product release has been overcome. Other highlights include synthesis of organic molecules using N₂ and CO as building blocks, the diatomic molecules with the two strongest bonds in chemistry.

Bimetallic Catalysts for Heterocycle Transformations: Energy Efficient Routes to Monomers and Chemical Feedstocks

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Funding: \$380,000 (2014-2016)

PROGRAM SCOPE

The goal of this research proposal is the development of new catalysts for carbonylation and rearrangements of heterocycles. The project focuses on two specific aims: 1) the development of the next generation of catalysts for enantioselective heterocycle carbonylation, and 2) the application of bimetallic catalysis in non-carbonylative reactions. The proposed work will focus on the development of new bimetallic catalysts for a broader range of reactions, including non-carbonylative transformations. The first specific aim is the development of enantiopure catalysts that can carbonylate epoxides and related heterocycles with control of absolute configuration of stereochemistry. Building on important discoveries during the last funding period, we will continue the development of catalysts capable of kinetic resolution of both *cis*- and *trans*-disubstituted epoxides. The resulting stereodefined molecules will be particularly interesting monomers for the synthesis of semi-crystalline aliphatic polyesters. A variety of methods—including *in situ* kinetic measurements, steric and electronic ligand variation, and DFT calculations—will be used to gain mechanistic insight and guide catalyst development. The second specific aim is the exploitation of bimetallic catalysts in non-carbonylative reactions. One main goal in this endeavor is to develop selective internal epoxide rearrangement to carbonyl compounds. The energy-efficient synthesis of environmentally benign materials from renewable resources is becoming increasingly important as fossil fuels become more limited and increasingly expensive. Carbonylation chemistry is an attractive synthetic route to monomers for biodegradable and biocompatible polymers and fine chemicals using biorenewable sources. Finally, we believe that the mechanistic information regarding bimetallic substrate activation and functionalization will have important broader impacts in the field of catalysis.

FY 2014 HIGHLIGHTS

A new enantiopure Lewis acid/carbonyl cobaltate carbonylation catalyst was discovered and applied to the regiodivergent carbonylation of racemic *cis*-disubstituted epoxides. The products were enantioenriched *trans*- β -lactones showing 90% ee or better, which were further elaborated into anti-aldol products in a one-pot sequence. The effectiveness of this new catalyst in inducing enantioenrichment was attributed to the *cis*- α coordination geometry of the ligand around the Lewis acidic metal-ion. Moreover, the reaction of *cis*-2-heptene oxide with the enantiopure catalyst was studied in detail to confirm that the epoxide underwent a regiodivergent carbonylation reaction. Lastly, regiodivergent carbonylation was applied to the synthesis of an important fragment of Globomycin. Future work will focus on the further development of enantioselective carbonylation catalysts as well as new reactions involving catalysts bearing enantiopure ligands.

Hydrocarbon, Oxidation, Dehydrogenation and Coupling over Model Metal Oxide Surfaces

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Funding: \$155,000 (2014)

PROGRAM SCOPE

This project is directed at understanding structure/function relationships in transition metal oxide surface chemistry, with an emphasis on chemistry related to the dehydrogenation and oxidation of small alkanes. Our work has focused on the surface chemistry of oxides of chromium, manganese and iron, with a current focused on manganese oxides. These neighboring fourth row transition metals allow access to oxides with metal atoms in 2+ and 3+ oxidation states (among others) with d electronic configurations ranging from d³ for Cr³⁺ to d⁶ for Fe²⁺. Because Cr₂O₃ and Fe₂O₃ have the same crystalline structural, it is possible to examine surface chemistry between these compounds where any differences in selectivity are strictly related to differences in d electronic configuration and not geometric (atomic) structure. These oxides and their combinations are members of a class of reducible oxide materials important for a variety of applications in catalysis because of the ability of surface cation sites to cycle between different oxidation states (primarily 3+ and 2+). Chemistry on model (single crystal) oxide surfaces is being investigated using the tools of UHV surface science for insight into the surface properties that control selectivity in oxidation, dehydrogenation, and coupling (C-C bond formation) reaction pathways of small hydrocarbons over iron oxides. Temperature programmed desorption (TPD) is being used to investigate the reaction pathways of hydrocarbon oxygenates (alcohols, carboxylic acids, etc.) and hydrocarbon halides (iodides, chlorides, etc.) Dissociative adsorption of these molecules provides access to oxygenated surface intermediates and hydrocarbon fragments which can be used to examine the site requirements for selective and non-selective hydrocarbon oxidation, dehydrogenation, coupling, and oxygen insertion reactions. Synchrotron-based photoemission and NEXAFS measurements are planned to characterize the surface intermediates.

FY 2014 HIGHLIGHTS

The preparation and characterization of different manganese oxides on MnO(100) has been investigated spectroscopically and with TPD of a variety of probe molecules. Mixed valence Mn₃O₄ is readily prepared by oxidation, but accessing Mn₂O₃ is difficult in vacuum via high temperature oxidation. Na incorporation during high temperature oxidation has also been found to stabilize the Mn in a 3+ oxidation state through the formation of NaMnO₂ surface layers. Fundamentals of the interaction of Na with MnO(100) in the absence of an oxidizing environment have also been examined. For low Na exposures, an irreversibly adsorbed monolayer of oxide-like Na is formed. Heating at temperatures above 450 K drives the Na subsurface, and heating to 1000 K causes a loss of Na in the surface region due to diffusion into the bulk MnO.

Moving to Sustainable Metals: Multifunctional Ligands in Catalytic, Outer Sphere C-H, N-H and O-H Activation

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Funding: \$160,000 (2014)

PROGRAM SCOPE

Catalysts for conversion of glycerol to lactic acid were found, a topic which proved acceptable to Nature Comm. Catalyst deactivation was of great interest, providing a number of metal clusters stabilized by NHCs rather than the conventional carbonyls. This was published by Angew Chem. A number of our catalysts proved useful for the Yale Solar team, who found that electrochemical activation gave the best results in water oxidation. A series of hydroxamate ligands proved to give highly unusual distorted structures with our Cp*Ir system; we hope these will prove active in cheap metal catalysis. Loss of Cp* was an unexpected activation pathway in a series of transfer hydrogenation catalysts. Two reviews on different aspects of catalyst deactivation were published in Chem Rev and J Organometal Chem. A heterogeneous Co-phosphine catalyst proved useful in a number of catalytic conversions although we are very puzzled how it works. Finally, a borohydride catalyzed hydrosilylation was discovered in applying a control reaction to a supposedly Ni-catalyzed reaction - in fact the Ni is not needed.

FY 2014 HIGHLIGHTS

The glycerol to lactic acid conversion is our top result this year; the energy relevance is that glycerol is a biodiesel byproduct and lactic acid is useful in numerous commercial applications.

Testing the Predictive Power of Theory for Determining the Structure and Activity of Nanoparticle Electrocatalysts

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Funding: \$200,000 (2014)

PROGRAM SCOPE

The objective of this research is to strengthen the correlation of experiment and theory as it relates to catalysis applications. Measurements of structure and catalytic activity of nanoparticles are related to theoretical calculations. This is done using dendrimer-encapsulated nanoparticles (DENS) as model electrocatalysts. Their small size of ~55-300 atoms, which corresponds to ~1-2 nm, allows for direct comparison to density functional theory (DFT) calculations performed on nanoparticles of the same number of atoms. This is an interesting size range because there are often large deviations from bulk behavior. With DENS, a small change in the number of atoms produces changes in the electrocatalysis results. By combining experiment and theory we not only validate theoretical models, we also gain a much deeper understanding of the structure/function relationship of DENS. To make theoretical activity predictions, a simple thermodynamic parameter is calculated and this is used as a representation of the overall reaction. This is often the binding energy of an adsorbate. Our research focus is on allowing theory to lead experiments, which will make it possible for calculations to predict the composition and structure of new and more active catalysts. For example, new catalyst candidates for the oxygen reduction reaction (ORR), hydrogen evolution reaction (HER), and CO oxidation were predicted during the past year. This was done by varying the composition of the DENS in an alloy-core@shell configuration. This catalyst architecture has many advantages. The noble shell enhances the durability of nanoparticles for catalysis and the alloy-core composition allows for fine tuning of the catalytic

properties. One such predicted case has been realized experimentally, and has therefore validated this approach for designing new catalytic materials.

FY 2014 HIGHLIGHTS

Catalytic materials containing an atomically thin Pt surface layer are a promising alternative to pure Pt nanoparticle catalysts for the oxygen reduction reaction (ORR). Pt-shelled catalysts can be stable, have significantly less Pt loading than commercial alternatives, and can exhibit higher activities. Recent progress has also been made using near-surface alloys to tune the activity of the catalytic surface. One such promising geometry is a monolayer shell covering a random alloy core of variable composition. These alloy-core@shell nanoparticles have both the robustness of core@shell structures and the tunability of random alloy particles. In a recent study, we predicted ORR activity trends of 2 nm alloy-core@Pt-shell nanoparticles using density functional theory (DFT) calculations with oxygen binding as the reactivity descriptor. The combination of Au and Pd in the nanoparticle core was found to be particularly interesting because variations of the core composition between pure Au and pure Pd are calculated to shift the oxygen binding on the Pt shell to values both weaker and stronger than bulk Pt. Our predicted trends in ORR activity, as well as the optimal core composition, provided a testable model for experiments. Accordingly, we synthesized and characterized dendrimer-encapsulated nanoparticles having the general structure AuPd@Pt, and then measured the electrochemical ORR reaction rates. The experimental findings were in nearly exact agreement with theoretical predictions over the entire range of core compositions. As predicted by theory, the composition Au_{0.28}Pd_{0.72}@Pt was found to have a higher activity for the ORR than even pure Pt. The ability to predict systematic tuning of catalyst performance and then test these predictions using fairly simple synthetic methods is a significant advance forward in the field of catalysis.

Modeling of Late Transition Metal Catalysts for Energy Applications

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

The major goals of DOE-BES supported research in the Cundari Group are to study the structure and reactivity of novel and emerging ligand systems in catalysis; to model novel catalysts for olefin hydroarylation; to identify mechanisms of group transfer by late transition metal complexes as a route to more efficient use of hydrocarbon feedstocks; and, to integrate modern computational chemistry research with the work of leading experimental groups and fellow DOE-BES contractors to better understand mechanisms and intermediates of transition metal catalysis pertinent to the DOE research mission.

FY 2014 HIGHLIGHTS

The most exciting research highlight of the FY 2014 has been the elucidation of the mechanism of action of promising catalysts for the direct production of styrene from benzene and ethylene. Most

ethylbenzene – which is produced on an enormous per annum scale in the U.S. – is then oxidized to styrene. A process for the direct production of styrene that could circumvent the ethylbenzene intermediate would be a major practical and fundamental breakthrough in catalysis. Initial work on related hydroarylation catalysts were carried out by two former Cundari Group members - Mr. (now Dr.) Bruce Prince and Mr. (now Dr.) Manny Gonzalez - for first-generation Pt(II) catalysts. We have sought to leverage these advances in the study of improved Rh(I) catalysts. The computational studies in our lab are being carried out in conjunction with long-term collaborator and fellow DOE-BES grantee, Prof. T. Brent Gunnoe at U. Virginia.

Sub Nanometer Sized Clusters for Heterogeneous Catalysis

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Funding: \$550,000 (2014-2016)

PROGRAM SCOPE

The focus of this project is the synthesis, characterization and reactivity of transition metal moieties ranging from single atoms to clusters of about 1 nm in diameter that are present on high surface area supports. A major barrier in the utilization of sub-nm clusters is that they are subject to Ostwald ripening, leading to growth in size to form nanoparticles. Previous work suggests that trapping single atoms on the support could help to slow the rates of ripening. Transition metals that are bound to the support through a covalent bond (for example M-O-S, where S is the support) would be expected to be more stable than zero-valent transition metal atoms. Hence, one of the goals of this project is the creation of suitable anchoring sites on high surface area catalyst supports. Conventional (non-reducible) oxide supports provide only limited number of sites to anchor ionic species. Reducible oxides provide many more sites for anchoring due to the presence of defects, such as vacancies. But reducible oxides are often not available in high surface area form, and they may not be as robust (can react to form carbonates, for example, or sinter easily) compared to the commonly-used high surface area supports such as silica, alumina, or carbon. Increasing atomic trapping sites on conventional catalyst supports is therefore important for improving the stability of sub-nm metal clusters on a supported catalyst. Another goal of this project is to expand the applicability of single atom catalysts to a broader class of catalyzed reactions. Transition metals in ionic form are perfectly situated for further manipulation of their catalytic activity by use of ligands, as in homogeneous catalysis. Understanding the principles that help in the design of robust single atom catalysts is one of the research challenges that is addressed in this project.

FY 2014 HIGHLIGHTS

Low temperature CO oxidation performance is important for meeting DOE goals for more efficient combustion engines. Metallic Pd is poisoned by CO at low temperatures. We have identified a novel pathway for CO oxidation on atomically dispersed ionic Pd sites which are present even on industrially-relevant gamma alumina. Aberration corrected STEM confirms the presence of isolated Pd species on alumina supports. The presence of La on the alumina, which is added to improve the hydrothermal stability of the alumina, results in enhanced stability of the ionic Pd species. Our proposed reaction

mechanism involves oxygen coming from the lattice, as shown by DFT calculations. The ionic Pd bound to alumina activates CO which then picks up a lattice oxygen. The vacancy site then adsorbs dioxygen, a second CO picks up the extra O, and the cycle repeats itself. Atomically dispersed Pd species show a positive order of reaction in CO, very different from that on metallic Pd. In a second project, we investigated the manipulation of Fe catalysts by the addition of Pd. A series of Pd/Fe₂O₃ catalysts were synthesized, characterized, and evaluated for the hydrodeoxygenation (HDO) of m-cresol. It was found that the addition of Pd promotes the catalytic activity of Fe while the product distributions resemble those of monometallic Fe catalysts, showing high selectivity towards the production of toluene (C-O cleavage without saturation of aromatic ring and C-C cleavage). A possible mechanism, including Pd assisted H₂ dissociation and Pd facilitated stabilization of metallic Fe surface as well as Pd enhanced product desorption, was proposed to be responsible for the high activity and HDO selectivity in Pd-Fe catalysts. The synergistic catalysis derived from the Pd-Fe interaction proved to be applicable to other precious metal promoted Fe catalysts, providing a promising strategy for future design of highly active and selective HDO catalysts using earth abundant Fe.

EARLY CAREER: Natural Catalysts for Molten Cellulose Pyrolysis to Targeted Bio-Oils

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Funding: \$320,000 (2014-2015)

PROGRAM SCOPE

Lignocellulosic biomass heated above 400 degrees Celsius thermally degrades to a short-lived liquid mixture which can be upgraded to liquid transportation fuels. In this work, we understand the fundamental reaction chemistry of degrading biopolymers and evaluate the role of inorganic catalysts on directing the pyrolysis chemistry to improved fuel precursors. The degradation of large biopolymers occurs via two sets of chemistries that we have previously described: (a) primary reactions break down biopolymers to volatile compounds, which can evaporate, while (b) secondary reactions are the conversion of volatile compounds within the biopolymer melt prior to evaporation. Inorganic catalytic materials are primarily capable of interacting with mobile chemical species within molten biopolymers, which means that they have the potential to catalyze desirable secondary pyrolysis reactions. Targeted secondary catalysis reactions include catalytic reduction and/or defunctionalization to produce chemical targets with unreactive functional groups.

FY 2014 HIGHLIGHTS

In 2014, we discovered the first catalytic method for tuning the pyrolysis of lignocellulosic biomass to desirable fuel precursors prior to vapor product formation. Inorganic catalytic materials are primarily capable of interacting with mobile chemical species within molten biopolymers, which means that they have the potential to catalyze desirable secondary pyrolysis reactions. With this insight, we selected furan decarbonylation as the target chemistry to evaluate the potential for selective secondary catalysis within biopolymer melts. Results indicated that supported metals including Pd and Pt on carbon, silica or alumina supports can dramatically alter the distribution of pyrolysis products. Evaluation of a range of experimental conditions discovered that up to 90% of furan carbonyl groups could be eliminated via

catalytic impregnation of Pd/C catalysts. This fundamental insight will be valuable for developing a catalytic technology to produce stable pyrolysis oils which can serve as a replacement for petroleum.

Structure and Function of Supported Base Catalysts

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Funding: \$165,000 (2014)

PROGRAM SCOPE

Solid bases are heterogeneous catalysts that have not been broadly exploited compared to solid acids. Thus, much of our effort over recent years has been focused on understanding how a variety of solid bases, including metal oxides, mixed metal oxides and zeolites, function as catalysts in chemical transformations. Our recent work with transesterification and Guerbet reactions, however, suggests that materials with surfaces exposing appropriately co-located acid and base sites are superior catalysts compared to materials traditionally considered as solid bases. In this project, the concept of acid-base cooperativity is being evaluated on catalysts for C-C bond forming reactions such as alcohol coupling and aldol condensation. Given the increasing production of ethanol in the US and elsewhere using non-traditional sources of carbon, a better understanding of the catalytic transformations of ethanol is needed. The specific objectives of this project are to synthesize acid-base bifunctional solid catalysts, to characterize their surfaces by adsorption microcalorimetry and IR spectroscopy of adsorbed bases, acids and amphoteric molecules, and to evaluate the reactivity of the bifunctional catalysts in steady-state and transient ethanol coupling reactions as well as model aldol condensation and alcohol dehydrogenation reactions.

FY 2014 HIGHLIGHTS

We have made substantial progress with understanding the acid-base nature of hydroxyapatite relative to magnesia and zirconia, and how that nature influences activity in the Guerbet coupling reaction. In particular, DRIFTS and adsorption microcalorimetry of acid-base probe molecules provided an excellent ranking of surface affinity for various types of adsorbates. We have also utilized isotopic transient analysis to evaluate the surface coverage of intermediates leading to butanol during the steady state reaction over magnesia and hydroxyapatite, as well as estimate the intrinsic turnover frequency of the catalytic cycle.

Towards Rational Nanoscale Control of Catalysis: A Fundamental Study of Zeolite Structure and Nucleation

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Funding: \$160,000 (2014)

PROGRAM SCOPE

Our goal is to employ the database of zeolite-like materials, and to develop and employ OSDA prediction and design methodology. We work with our theoretical colleagues to screen the database for interesting and useful physiochemical functions. We have worked with several academic groups to help them use this database. At present, roughly a dozen academic groups are using this database. This database is now being screened by colleagues at Georgia Tech (David Scholl), Berkeley (Berend Smit), Northwestern (Randy Snurr), Princeton, BASF, Chevron, and others. We have developed a computational procedure to predict chemically synthesizable organic structure directing agents for zeolites [2]. A major tool to influence zeolite nucleation and growth is the use of organic structure directing agents (OSDAs). These OSDAs must be soluble in the synthesis medium. They must also be stable under synthesis conditions. The OSDAs are occluded during the zeolite growth process, so they must fit geometrically within the zeolite. The OSDA must additionally interact with the zeolite framework with favorable energetics. We have applied this methodology to develop an OSDA to make HPM, a very interesting chiral zeolite, in collaboration with Mark Davis at Caltech, and the first successful synthesis of a specified molecular sieve through the use of an OSDA that is predicted from a recently developed computational method that constructs chemically synthesizable OSDAs. The general methodology demonstrated here to create STW may lead to new, simpler OSDAs for existing frameworks as well as a method to predict OSDAs for desired, theoretical frameworks. Two additional zeolites have been made by this approach.

FY 2014 HIGHLIGHTS

- 1) Synthesis of HPM, a very interesting chiral zeolite, in collaboration with Mark Davis at Caltech [5], and the first successful synthesis of a specified molecular sieve through the use of an OSDA that is predicted from a recently developed computational method that constructs chemically synthesizable OSDAs.
- 2) Explanation of long-standing conundrum of why there are so few 7-membered rings in known zeolites: the constraint of proximity to the low-density edge of predicted structures is what leads to a low probability of 7-membered rings.
- 3) Analysis of the ADOR transformation, showing that the preferential location of Ge in the double four-membered rings (D4R) of zeolite can be explained with periodic density functional theory calculations.
- 4) We identify, through a large-scale, multi-step computational screening process, promising zeolite structures for two energy-related applications: (i) purification of ethanol beyond the azeotropic limit in a single separation step from fermentation broths and (ii) two orders of magnitude better adsorption characteristics than current technology for linear and slightly branched alkanes with 18-30 carbon atoms encountered in petroleum refining.

Publications:

- 1) J. E. Schmidt, M. W. Deem, and M. E. Davis, "Synthesis of a Specified, Silica Molecular Sieve using Computationally Predicted Organic Structure Directing Agents," *Angew. Chem. Int. Ed.* 53 (2014) 8372-8374
- 2) X. Li and M. W. Deem, "Why Zeolites Have So Few 7-Membered Rings," *J. Phys. Chem. C* 118 (2014) 15835-15839
- 3) S. O. Odoh, M. W. Deem, and L. Gagliardi, "Preferential Location of Ge in the UTL and IPC-2a Zeolites," *J. Phys. Chem. C* 118 (2014) 26939-26946.

- 4) P. Bai, M.-Y. Jeon, L. Ren, C. Knight, M. W. Deem, M. Tsapatsis, and J. I. Siepmann, "Predictive Materials Discovery: Finding Optimal Zeolites for Challenging Separations and Chemical Conversions," Nature Comm., to appear.

Catalyst Design by Discovery Informatics

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Funding: \$700,000 (2014)

PROGRAM SCOPE

Our overall goal is the development of a new paradigm for catalyst discovery and optimization through Discovery Informatics, a model-based approach to catalyst design. To reach this objective, we are developing experimental and computational tools to create an information-rich database from which chemical descriptors and appropriate models can be identified. Our vehicle for heterogeneous catalysis is the water-gas shift (WGS) reaction for which we have kinetic and chemical characterization data on over 800 supported metal catalysts. Analysis of this database identifies WGS as a dual functional reaction and has focused our attention on the metal-support interface, which we are now modeling with density functional theory to understand and predict the chemistry the active catalytic sites it generates. For homogeneous catalysis, our test bed is single site olefin polymerization. Here we have developed software to facilitate the building of population balance kinetic models that allow inclusion of a variety of elementary kinetic steps to predict molecular weight distribution (MWD) as well as monomer loss, end-group identity resulting from chain termination, and number of active sites. Analysis of kinetic parameters obtained from fitting a rich set of data for families of catalysts has allowed us to identify kinetic mechanisms and steric and electronic descriptors that predict catalytic activity within families.

FY 2014 HIGHLIGHTS

We have correlated the increase in WGS rate and strong effects of Fe on both the activation energy and the CO order of reaction for Au on Fe-doped TiO₂ to the influence of Fe on the CO bonding to metal sites. Removal of Co from PtCo/MWCNT shows, on the other hand, that oxidized Co is the source of promotion and does so by enhancing dissociation of water. The unusually high rate for Pt or Au supported on Mo₂C is accounted for by promotion CO activation by the metal to enhance reaction with OH provided by the carbide support. A DFT study of WGS on Pd and Pt (111) surfaces confirms the importance of the carboxyl pathway and shows that: i) the metal alone cannot account for experimental results on supported metals, and ii) that coverage effects of the CO binding energy are important and can be accounted for with a new cluster expansion approach. Calculations on metal nanowire models of Pt on Al₂O₃ and Au on MgO confirm the carboxyl kinetic model and show enhanced H₂O activation at the metal/oxide interface and CO bonded to interfacial metallic sites. Applications to homogeneous

catalysts have moved to non-Cp coordination catalysts for olefin polymerization and oligomerization. We have discovered the importance of a binuclear catalyst complex to account for changes in rate and MWD at sub-stoichiometric activator conditions and correlated effects of the pendant group on several rate constants with corresponding changes in HOMO energy. Observation of a unique structural window as a function of pendant chemistry for oligomer formation, extraction of activation energies from the temperature dependence of the reaction network rate constants, comparison of the kinetic consequences of Ti, Zr, and Hf in a family of catalyst complexes, and co-polymerization of 1-hexene with styrene are currently being vigorously pursued. Kinetic modeling capabilities have been expanded with a new algorithm based on Dynamic Monte Carlo methods.

Control of Reactivity in Nanoporous Metal/Ionic Liquid Composite Catalysts

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Funding: \$150,000 (2014)

PROGRAM SCOPE

In this proposal, we have been examining a new concept in nanostructured heterogeneous catalysis design – the ionic liquid (IL)/nanoporous metal (NPM) composite. The idea behind this structure is to tailor the chemical environment within the pores of a metallic electrocatalyst in order to enhance the aggregate composite activity; the mechanisms of enhancement being (a) bias of mass transport of reactants to the surface and products away from it, and (b) corralling of reactants and products to spatially separate them and reduce side reactions. We have made a particular focus on aqueous electrocatalysis under kinetically limited conditions, and in which the catalyst is a nanoporous metal and the biasing environment is an ionic liquid impregnating the pores. Of particular interest will be the electroreduction of gaseous species, primarily oxygen, at nanoporous electrodes separated from an aqueous phase by a thin ionic liquid layer. In typically aqueous electrocatalysis, reactivity is often limited by solubility of the gas in the aqueous (acid or base) phase. By using a hydrophobic ionic liquid with higher gas solubility than the aqueous phase, a diffusive driving force is added to the reaction driving force, biasing the gas to remain near the catalyst surface and increasing activity; activity is further enhanced if the ionic liquid has little solubility for the products. For oxygen reduction in acids, this concept has led to significant improvements in aggregate mass activity. Conversely, creation of new aprotic ionic liquids will be examined with an eye toward creation of reactive intermediates (e.g., peroxide or superoxide) species that can be made under electrochemical conditions that normally lead to hydrogen evolution or water reduction. These are being used for secondary oxidation reactions as they diffuse back into the aqueous phase, but in an orderly manner, without hydrogen evolution or production of other unwanted reduced species.

FY 2014 HIGHLIGHTS

Over the last year a critical technical accomplishment has been the development of a flow cell that allows the study of nanoporous Pt/Ni impregnated with hydrophobic ionic liquid catalysts with controlled amounts of ionic liquid. As a result, we have been able to perform a survey of ionic liquids properties and how they impact composite catalyst behavior for the oxygen reduction reaction. These

properties include oxygen solubility, viscosity, (a)proticity, ionic conductivity, and water solubility. Oxygen solubility turns out to be quite important, helping draw reactants to the catalyst surface. Interestingly, we also find that water solubility very critical. Ionic liquids with low water solubility lead to proton-diffusion limited reaction kinetics, which have never been observed in oxygen reduction studies before. This observation has led to elucidation of a new kinetic regime for reduction reactions, in which there is faster transport of reactants to catalytic surfaces than protons, which kinetically suppresses hydrogen evolution. This general result will now be applied to the reduction of other gaseous species.

EARLY CAREER: Bond-Formation and Catalysis by Base-Metal Unsaturated Isocyanides

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Funding: \$150,000 (2014)

PROGRAM SCOPE

This DOE Early Career Research Program Award seeks to develop and understand small-molecule-activation catalysis by base-metal unsaturated isocyanide complexes. The project is focused in two specific areas: 1) the development and mechanistic delineation of carbon dioxide (CO₂) reduction by manganese (Mn) m-terphenyl isocyanide electrocatalysts and 2) discovery of new bond construction and cleavage reactions by low-valent, low-coordinate m-terphenyl isocyanide complexes of cobalt. For specific area #2, CO₂ activation by one- and/or two-electron processes is also a primary goal. The development of catalytic and/or stoichiometric CO₂ activation schemes based on base-metal systems is being pursued as an effort to mitigate costs associated with precious metal mediated catalysis. In order to provide an electronic environment for base metals mimicking that traditionally found in the precious metals, strong-field m-terphenyl isocyanide ligands are employed throughout this work. This ligand class has several other advantages, including: (a) facile steric and electronic modification through synthesis and (b) convenient spectroscopic markers for the characterization of catalysts and intermediates, as well as for measurement of reaction progress. For specific goal #1, the ultimate outcomes of this work are the discovery of inexpensive, well-defined CO₂-electrocatalysts that operate efficiently at low over-potentials and a detailed analysis of their mechanism of catalysis. For specific goal #2, the ultimate outcomes of this work entail the discovery of new transition metal-mediated bond-activation paradigms in homogeneous solution.

FY 2014 HIGHLIGHTS

The most significant accomplishment during fiscal year 2014 was the isolation, detailed characterization and exploration of the reaction chemistry accessible to of the manganese monoradical complex Mn(CO)₃(CNAr^{Dipp2})₂. This species is a key intermediate in Group 7 metal electrocatalytic CO₂ reduction sequences and is the first to be isolated and studied in detail by a complement of spectroscopic and synthetic techniques. This monoradical displays an intriguing reaction chemistry with a diverse host of substrates. For example, reactions between Mn(CO)₃(CNAr^{Dipp2})₂ and nitrosoarenes result in the formation of side-on bound nitoxide radical ligands, which is in direct contrast to the chemistry reported for other, unstable, zero-valent Mn monoradicals. It was also shown that Mn(CO)₃(CNAr^{Dipp2})₂ species is not competent for CO₂ activation, which is a main finding of the work. The interconversion between

$\text{Mn}(\text{CO})_3(\text{CNAr}^{\text{Dipp}2})_2$ and the mono-hydride complex $\text{HMn}(\text{CO})_3(\text{CNAr}^{\text{Dipp}2})_2$ was also explored in detail and it is shown that neither complex is a major contributor to a productive CO_2 reduction sequence. In addition to a delineation of the chemistry accessible to $\text{Mn}(\text{CO})_3(\text{CNAr}^{\text{Dipp}2})_2$, fiscal year 2014 included significant synthetic and spectroscopic efforts leading to an extensive library of electronically diverse *m*-terphenyl isocyanide ligands. As a result of this study, topological and electronic criteria have been established for the construction of isocyanide ligands that present a significant π -acidic ligand field akin to carbon monoxide (CO), but that also promote coordinative unsaturation.

Supported Nanocluster Catalyst Formation in Contact with Solution: Kinetic, Mechanistic and Synthetic Fundamental Studies

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Funding: \$163,000 (2014)

PROGRAM SCOPE

The primary scope of our DOE-funded program is to examine and establish the kinetics and mechanism(s) of the nucleation, growth and agglomerative formation of supported-nanoparticle heterogeneous catalysts. One specific goal is to learn how to transfer the synthetic and mechanistic insights—that have been gained from the modern revolution in nanoparticle synthesis, characterization, and catalysis in solution—to the preparation of the next generation of improved, more selective, more active and longer-lifetime, solid-state supported-nanoparticle heterogeneous catalysts that are the primary type of catalyst used in commercial manufacturing.

FY 2014 HIGHLIGHTS

Five papers and one Ph.D. thesis were published during the 2013-2014 period. Significant among those is a paper “A Four-Step Mechanism for the Formation of Supported-Nanoparticle Heterogeneous Catalysts in Contact with Solution: The Conversion of $\text{Ir}(1,5\text{-COD})\text{Cl}/\gamma\text{-Al}_2\text{O}_3$ to $\text{Ir}(0)_{-170}/\gamma\text{-Al}_2\text{O}_3$ ”. This paper reports a new, unique mechanism for the formation of heterogeneous catalysts and for two basic steps in nanoparticle catalyst sintering—sintering being crucial to catalyst lifetime and, therefore, overall catalyst productivity and commercial value. Also published were two papers supporting a DOE Graduate Fellow and his work in the forefront area of water-oxidation catalysis (WOC), a catalytic reaction central to our secure energy future. That work determines the true catalyst in water-oxidation catalysis beginning with discrete metal-oxide precatalysts called polyoxometates, currently some of the most promising precatalysts in the WOC area. A critical review of the literature of polyoxometalates as water oxidation precatalysts was also written. Finally, a very important paper was written detailing that nucleation of the formation of $\text{Ir}(0)_n$ nanoparticles is, contrary to literature expectations, a simple second-order kinetic process in the concentration of the precursor, $[(1,5\text{-COD})\text{Ir}^I \cdot \text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]^{8-}$. This is arguably a ground-breaking result, since it teaches that the previously widely used Classical Nucleation Theory, which predicts a nucleus much larger than two (Ir_n , $n \gg 2$), is not correct in at least this case. Given that nucleation is the key initial process underlying phase changes throughout nature, this finding has potentially very broad implications, specifically that very small nuclei, of even 2-3 monomers of the precursor phase, may be sufficient to nucleate the formation of new phases.

Atomically Dispersed Metal Surface Species As Catalysts for Alcohol Conversion, Hydrogen and Chemicals Production

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Funding: \$580,000 (2014-2016)

PROGRAM SCOPE

Isolated metal ion-centric sites stabilized on supports by $-O$ ligands were identified first in this project as the active sites for the water-gas shift reaction. This is true for both gold and platinum. Alkali addition is used to stabilize the active $Pt-O(OH)_x$ - or $Au-O(OH)_x$ - species on any support, including zeolites and mesoporous silica. The intrinsic activity is specific to the metal and invariant to the support type or alkali addition. These atom-centric species may catalyze other reactions. We have already demonstrated the $Au-O_x$ centers as catalysts for the methanol steam reforming reactions, and presently investigate ethanol reactions. Metals of interest include Au, Pd, and Cu on supports of tunable basicity, such as $ZnO-ZrO_2$, on which the metals can be dispersed atomically and the yields of desired valuable chemicals and hydrogen be maximized. A second major goal of the project is to develop single atom alloy (SAA) combinations, the first of which (PdCu) we have recently reported to be highly active and selective for the hydrogenation of alkynes. We have shown this both with model catalysts, e.g. Pd atoms deposited in Cu(111) in UHV, and with their nanoparticle SAA analogs, i.e. Pd atoms deposited in Cu nanoparticles and tested at ambient pressure, thus “bridging” the pressure and materials gap between surface science and catalysis. The information obtained from atomic-resolution STM is crucial for understanding and designing new catalysts; while the catalytic information drives the examination of new model catalysts in the UHV systems. Reactions of interest include selective hydrogenation of dienes and selective oxidation of alcohols on PdCu, PtCu, and PdAu. Development of atomic-scale catalysts will fulfill a long-standing DOE goal in catalysis; i.e. the achievement of efficient resource utilization and energy-efficient processes. The systems we investigate greatly reduce the use of expensive platinum group metals and demonstrate maximum atom efficiency.

FY 2014 HIGHLIGHTS

In several papers and review articles published this year, we have generalized our findings of single-site isolated metal ions held by $-O$ ligands on supports as the active sites for the water-gas shift reaction. In addition to the usual “active” oxide supports, “inert” supports as diverse as carbon nanotubes, zeolites, and mesoporous silica were used in order to demonstrate that a similarly structured single-site $M-O(OH)_x$ species is the catalytic site on any support. Inert supports may be used only with alkali ion addition. The alkali ions form a shell around the Pt or Au atoms, binding them through $-O$ ligands, and supplying the regenerable $-OH$ needed for the reaction. The apparent activation energy of the reaction is characteristic of the $M-O(OH)_x$ site, not the type of support; it is also invariant to the presence of the alkali. Hence, we can design such catalysts on Earth-abundant supports, while using only trace amounts of the precious metals. In other work, we reported that atomically dispersed gold in $ZnO-ZrO_2$ surfaces catalyzes with 100% atom efficiency the methanol steam reforming reaction, and the production of

acetone from ethanol at low temperatures. Working with single atom alloys, we have demonstrated that very low concentrations of individual, isolated Pt atoms in a Cu surface catalyze the industrially important selective hydrogenation of butadiene to butenes. Our experiments show that Cu binds butadiene weaker than Pt, but in nanoparticle systems the dissociation of molecular H₂ is often the rate limiting step on Cu. We have used a surface science and microscopy approach to interrogate the atomic geometry of Pt-Cu alloys. We discovered the minimum ensemble of Pt, a single atom, embedded in Cu(111) single crystal surfaces will dissociate H₂. Furthermore, isolated Pt atom geometries, unlike continuous Pt ensembles, are resistant to poisoning and maintain activity after many hydrogenation cycles.

Molecular-Scale Understanding of Selective Oxidative Transformation of Alcohols Promoted by Au and Au-Based Alloys

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Funding: \$183,000 (2014)

PROGRAM SCOPE

The project focuses on detailed mechanistic understanding of reactive processes –both for discovering new processes and for controlling selectivity in known reactions—using gold-based alloys as prototypes. We will focus on several key chemical processes that collectively illustrate a rational basis for the design of new catalytic materials and processes involving functionalization of alcohols and polyols: selective oxidation, amide synthesis, carbonylation, and alkylation. These processes were selected because they all have high value in chemical production and provide a foundation of knowledge for efficiently synthesizing key platform chemicals. Our objectives are (1) to understand and manipulate the key elementary steps in these potentially sustainable catalytic processes via studies with model systems and (2) to visualize and image these materials and reactions in order to provide a molecular picture of key catalytic studies. The proposed research is centrally related to the DOE-BES mission as articulated in several BES reports, including “New Science for a Secure and Sustainable Energy Future” and “Catalysis for Energy”. These reports emphasize the need for fundamental research in energy research, including the need to fabricate, design, characterize, and assemble new structures, including nanoscale alloys for energy-related applications.

FY 2014 HIGHLIGHTS

Significant advances in understanding important organic coupling reactions on oxygen-activated Au have been made in the project over the past year toward the overall objective of increasing reaction selectivity. Key results that advanced understanding of catalytic processes are: (1) development of a paradigm for predicting a hierarchy of binding affinity of important key reactants that includes binding of the primary functional group but also demonstrates the importance of weak (van der Waal’s) interactions between organic groups and the surface; (2) demonstration of the dependence of adsorbate stability on the coverage of adsorbed oxygen on Au—high O coverages destabilize strongly-bound acetate, for example. These principles have been tested in a variety of different reaction systems, including production of alkoxides and ethers via addition of alkyl groups to O on gold, alcohol coupling

reactions to form methyl esters, displacement and removal of strongly-bound poisons, e.g. carboxylates, from the surface, and investigation of the effect of fluorination on binding to the surface and on selective oxidation processes. We have also investigated model Ag/Au alloys and demonstrated that mixed Ag-Au sites exhibit different kinetics for both O recombination and for methanol coupling to methyl formate. This work is a springboard for understanding alloy materials more generally. Most recently, we have been able to image oxygen bound to Au(110) on an atomic scale along with reactive intermediates formed from reaction with the adsorbed O. These studies will provide us with molecular scale insight into how reactive species distribute themselves on the surface in order to assess the potential role of intermolecular interactions on their stability and reactivity. Our work establishes key paradigms for controlling reaction selectivity for complex processes on gold.

Activation of Carbohydrates for Applications in Biofuels and Biofeedstocks

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Funding: \$150,000 (2014)

PROGRAM SCOPE

The goal is to develop new methods for the activation of carbohydrate C-O bonds for the synthesis of value added compounds and biofuels. One focus is on the reduction of silane-protected C-O bonds through the catalytic activation of silanes to generate an available hydride equivalent and a Lewis acidic silyl cation, which together provide a means for carbohydrate C-O bond reduction. Expanding this system to include deoxygenation of alcohol containing polymers to generate new polymeric materials is also included. Carbohydrate protecting group compatibility (i.e. acyl protecting groups) for wider application is a second focus. Lastly, the utilization of stoichiometric Lewis acids along with a competent aromatic nucleophile for the generation of C-aryl glycosides is also under investigation.

FY 2014 HIGHLIGHTS

$B(C_6F_5)_3$ -catalyzed hydrosilylative reduction of carbohydrates. We previously reported the complete reduction of glucose and methyl glucoside to a mixture of hexane and hexene isomers. This conversion of biomass was catalyzed by a cationic iridium complex supported by a tridentate POCOP ligand, and diethylsilane (Et_2SiH_2) provided the requisite hydride. More recently, we observed that the hydrosilylative reduction of monosaccharides, oligosaccharides, and even polysaccharides can be catalyzed by a non-metallic commercially available Lewis acid, specifically tris(pentafluorophenyl)borane, $B(C_6F_5)_3$. This potent catalyst allows the reduction to proceed even faster than the iridium-based catalyst, providing shorter reaction times (ca. 1 hour vs. 1 day for the iridium catalyst) and reducing a wider range of biomass-derived substrates including methyl cellulose. This work has now been published in *Angewandte Chemie* (Adduci, L. L.; McLaughlin, M. P.; Bender, T. A.; Becker, J. J.; Gagné, M. R. *Angew. Chem. Int. Ed.* 2014, 53, 1646–1649). To expand the utility of this methodology, we next targeted selective catalysis. We envisioned that cleaving some but not all of the carbon-oxygen bonds of carbohydrates would allow us to generate valuable feedstocks from inexpensive biomass sources by preserving some of the inherent chirality of carbohydrates. Gratifyingly, selective deoxygenation was achieved using bulkier tertiary silanes, namely dimethylethylsilane (Me_2EtSiH) and

triethylsilane (Et_3SiH), in place of the less bulky secondary silane Et_2SiH_2 . This work is currently being prepared for submission to Nature: Chemistry. It will be a high impact publication.

Dispersed Metal Cluster Catalysts by Design: Synthesis, Characterization, Structure and Performance

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

To better understand the class of supported metal cluster catalysts and to lay a foundation for the prediction of properties leading to improved catalysts, we have synthesized metal catalysts with well-defined structures and varied the cluster structures and compositions systematically—including the ligands bonded to the metals. These ligands include supports and bulky organics that are tuned to control both the electron transfer to or from the metal and the accessibility of reactants to influence catalytic properties. We have developed novel syntheses to prepare these well-defined catalysts and applied spectroscopic, microscopic, and computational methods to determine their structures, reactivities, and catalytic properties. The supports as ligands range from nearly flat MgO surfaces to silica to enveloping zeolites, and we use bulky calixarenes to provide controlled coverages of the clusters. We are working to achieve a deep, fundamental understanding of how to synthesize robust supported and ligand-modified metal clusters with controlled catalytic properties, thereby bridging the gap between active site structure and function in unsupported and supported metal catalysts. We are also investigating zeolites as catalysts and supports and investigating their delamination by determining tomographic TEM images. We have also used spectroscopy, scanning transmission TEM, and rates of cyclohexene hydrogenation as a reporter reaction (with Prof. R. Finke) to track the genesis of supported iridium clusters.

FY 2014 HIGHLIGHTS

We synthesized coordinatively unsaturated tetrairidium clusters with CO and phosphine ligands, learning to stabilize them in a decarbonylated state by using bulky calixarene phosphine ligands. Tetrairidium clusters with these ligands bonded to 3 of the 4 Ir atoms were supported on silica, giving stable catalysts for H-D exchange and ethylene hydrogenation. Both vacancies at Ir atoms in the apical position and at Ir atoms in the basal plane of the tetrahedral clusters bond to CO and to hydrogen. However—because of strong electronic effects of the electron-donor phosphines, demonstrated by density functional theory—only the apical vacancy sites bond to ethylene, and they alone catalyze its hydrogenation. This is a new kind of single-site catalyst, and the fine control of catalytic properties makes one think of enzymes. We used computational chemistry to predict the reaction chemistry of these catalysts and a broad family of phosphine-substituted iridium clusters, showing that differences in relative energies are consequences of both electronic and steric effects of the ligands. Phosphines are σ -electron donors that lead to increased carbonyl ligand dissociation energies as more phosphines are substituted. The trend is clear in small clusters but not for tetrairidium. Kinetically, more phosphine

substitution leads to easier dissociation of carbonyls, which usually occurs at bridging positions. Among the best-defined supports for metal cluster catalysts are zeolites, and delaminated zeolites provide high surface areas. To understand the delamination process, we used 3-D imaging in scanning transmission electron microscopy to obtain tomograms on the nanoscale showing that the delamination proceeds through two distinct steps: chemical treatment that leads to a swelled material and a subsequent calcination that leads to curling and peeling off of delaminated zeolite sheets. The results are new in characterizing direct, local morphological changes accompanying delamination.

Single-Site Noble Metal Catalysts on Crystalline Supports: Synthesis, Structure, Characterization, and Performance

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Funding: \$185,000 (2014)

PROGRAM SCOPE

The simplest supported metal catalysts, like organometallics in solution, consist of single metal atoms stabilized by ligands, which include the supports. Researchers worldwide are paying increasing attention to these single-site catalysts, but there are a number of issues that are commonly glossed over, including the nature of the bonding of the metals to the supports, the oxidation states of the metals, and the ligands present on the metals. Our goals are to synthesize such catalysts precisely, with an emphasis on metals that are noble—because of their importance in technology—and supports that are crystalline—because their well-defined structures facilitate fundamental understanding of the catalytic species on them. Our characterization methods include IR, NMR, EPR, X-ray absorption spectroscopies, high-resolution STEM, and density functional theory. We developed novel syntheses to prepare these well-defined catalysts, applying spectroscopic, microscopic, and computational methods to determine their structures, reactivities, and catalytic properties. Our supports are zeolites and high-area crystalline MgO. By understanding the roles of the supports and other ligands, we have tuned the reactivities and catalytic properties of supported rhodium, iridium, osmium, and platinum complex catalysts. We believe that the emerging understanding of this class of catalyst is fundamental and deep, providing a firm basis for representation of the structures and reactivities by theory and a foundation for discovery of catalysts with new and useful properties. The data identify metal–support bonds and ligands on the metals; they demonstrate the uniformity of the supported species; they provide insight into the metal oxidation states; they determine reactions of the ligands and reaction intermediates, pointing the way to the design of active and selective catalysts.

FY 2014 HIGHLIGHTS

Our catalysts consist essentially of isolated metal centers on supports made by precise syntheses from metal complexes such as Rh(diethylene)(acac), Ir(diethylene)₂(acac), or Pt(diacac) reacting with the surface of a structurally well-defined high-area crystalline support, a zeolite or MgO. The supported catalysts are mononuclear, cationic metal complexes; the supports provide oxygen ligands to the metals, anchoring them to the surfaces. A reason for working with catalysts having such well-defined structures is that they are susceptible to exact structural characterization. The new structures offer new catalytic

properties—especially high selectivities, which (as in homogeneous catalysis) are associated with unique catalytic species and catalytic cycles that may be elucidated in depth. We used electron microscopy to resolve individual atoms of Ir, Os, Pt, Au, and even Rh on zeolites and MgO. We found zeolite-supported iridium complexes that form unique, new, rather stable dinitrogen complexes, which we have characterized. We synthesized isolated single rhodium complexes on supports and selectively converted them to rhodium pair sites, which have markedly different reactivities in reactions involving H₂. We found a stable site-isolated platinum complex catalyst for CO oxidation. We elucidated patterns of the reactivity of supported metal complexes that depend on the support and other ligands bonded to the metal, showing how these induce delinking from the support and lead to the first steps of cluster formation. A review summarizing our conception of the field and recent results appeared in *Accounts of Chemical Research*, 2014, 47, 2612.

Oxide-Metal Interactions Studied on Core-Shell Catalysts

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PROGRAM SCOPE

Precious metal catalysts are widely applied for pollution control in gasoline and diesel exhausts, as well as many other chemical processes. Catalyst stability and activity are serious issues that are not completely resolved, especially with new regulations planned for methane emissions. Developing catalysts with improved stability and activity remains an important goal that could have a very large commercial impact. We are synthesizing and characterizing core-shell catalysts in which the metal core is surrounded by a thin porous shell of a catalytically active oxide. We are interested in understanding how the oxide shell can modify the activity and stability of metal catalysts.

FY 2014 HIGHLIGHTS

Novel Pd-zirconia core-shell catalysts have been synthesized using self-assembly methods. These were then studied for methane oxidation and were found to be as active and more stable than the analogous Pd-ceria catalysts. Both catalysts showed nearly identical reaction rates and thermal stabilities under dry conditions but the Pd-zirconia catalysts were very stable in the presence of water vapor. Coulometric titration and pulse-reactor studies demonstrated that zirconia in contact with Pd can be reduced and that the Pd-PdO equilibrium at 873 K is shifted to much lower oxygen fugacities. Because PdO is more active for methane oxidation, this observation provides a possible explanation for the superior performance of the Pd-zirconia catalyst. Au-titania, Core-shell nanostructures were also synthesized and characterized for room temperature CO oxidation. The alumina-supported catalysts showed higher activity and thermal stability than conventional Au/TiO₂ samples and were able to maintain their activity and 3-nm Au particles size upon calcination up to 873 K. Furthermore, it was found that the crystallization of titania was suppressed in the core-shell structure, resulting in a thin layer of small titania particles, which is favorable for the dispersion and thermal stability of Au nanoparticles.

EARLY CAREER: Unifying Principles for Catalytic Hydrotreating Processes

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PROGRAM SCOPE

Fast pyrolysis of biomass, a renewable and sustainable resource, is a promising low-cost technology that produces bio-oil suitable for use as transportation fuel after an appropriate upgrade step. The upgrade can be achieved by reducing the high oxygen content of up to 35 – 40 wt.% through hydrotreatment over heterogeneous catalysts, but the complexity of bio-oils with ca. 400 different oxygenated compounds and the fact that this technology has only recently gained interest are both responsible for the lack of fundamental knowledge in this field. In contrast, the petroleum industry has been using hydrotreating reactors with cobalt and nickel promoted molybdenum sulfide based catalysts for the removal of sulfur impurities for decades, and the catalyst structure, nature of the active site, and elementary reaction steps are largely understood. This project builds on the hypothesis that the hydrotreating processes for the removal of oxygen and sulfur are fundamentally similar at the atomic-scale and existing knowledge from the treatment of petroleum derived feedstock can be leveraged for the design of novel catalysts for the upgrade of bio-oil. Electronic structure simulations on high performance computing infrastructure and kinetic modeling will be used to improve our mechanistic understanding of bio-oil hydrotreatment and to derive characteristic catalyst properties that are responsible for high activity and selectivity. From the resulting structure-function relationships we can extract common features of hydrotreating catalysts and develop unifying principles that lead to the accelerated design of novel materials for bio-oil upgrade.

FY 2014 HIGHLIGHTS

The highlights for this recently awarded grant cover the period from July 15 to September 30, 2014. We have started to compare the hydrodeoxygenation (HDO) pathway of furan with the well-studied hydrodesulfurization (HDS) pathway of thiophene on Ru and Mo oxides and sulfides. Our preliminary results indicate that the reaction pathways for HDO and HDS are similar, but not identical, which may be attributed to the different crystal structure of the corresponding oxides and sulfides. More detailed investigations are ongoing.

The fully DOE-funded graduate student Sashank Kasiraju presented the first set of results at the 2014 CAMD Summer School on Electronic Structure Theory and Materials Design, DTU, Kongens Lyngby, Denmark and won the 'Best Poster Award'. The poster was titled 'Hydrodeoxygenation of Furan versus Hydrodesulfurization of Thiophene: A First Principles Investigation' and was co-authored by the 2nd DOE-funded graduate student Byeongjin Baek. The poster award was also featured on the University of Houston - Chemical Engineering Department News website:

<http://www.egr.uh.edu/news/201410/chbe-student-wins-overseas-poster-contest>.

The results of this DOE project have also been included in 3 invited talks given by PI Grabow:

1. "Water mediated proton transfer at metal/metal-oxide interfaces" Symposium in honor of Prof. S. Linc receiving the ACS Catalysis Lectureship, ACS Fall Meeting, San Francisco, CA, August 11th, 2014.

2. "Mechanism and nature of the active site of Ru/TiO₂ for hydrodeoxygenation of acetaldehyde" Catalysis for Biomass Conversion Symposium, ACS Fall Meeting, San Francisco, CA, August 2014.
3. "Computational Design of Catalytic Materials for Fuels & Chemicals Production using Activity Descriptors" The DOW Chemical Company Seminar Series, Freeport, TX, July 31st 2014.

Development of Transition Metal Catalysts for the Functionalization of Carbon-Hydrogen Bonds: Fundamental Studies of Catalytic Hydroarylation of Olefins

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 Funding: \$150,000 (2014)

PROGRAM SCOPE

With increased global demand for fossil resources, new technologies that provide useful commodity chemicals at lower cost and with reduced environmental damage are a priority, especially efficient and clean utilization of hydrocarbons derived from petroleum and natural gas. At the center of almost any new technology for catalytic hydrocarbon manipulation is metal-mediated C–H activation, yet the catalytic functionalization of inert C–H bonds of hydrocarbons remains one of the foremost challenges facing synthetic chemists. The net addition of aromatic C–H bonds across olefin C=C bonds, olefin hydroarylation, provides an atom economical reaction with broad potential including applications in both commodity scale processes as well as fine chemical synthesis. We have been studying olefin hydroarylation catalyzed by well-defined transition metal complexes. In the past year, we have prepared and pursued catalysis with new complexes based on Ru(II), Pt(II), Fe(II), and Rh(I). These studies have led to the development of new molecular catalysts for the production of alkyl arenes and vinyl arenes, which are used in plastics, soaps and detergents and in fuels. A primary focus has been centered on developing mechanistic understanding of the catalysts, thus allowing rationale development of improved catalysts.

FY 2014 HIGHLIGHTS

Support from this DOE grant has resulted in the publication of six manuscripts during FY2014. We have developed a detailed understanding of the influence of ancillary ligand for Pt(II) catalyzed hydrophenylation of olefins using bis-nitrogen chelates. More strongly donating ligands increase catalyst longevity, which is proposed to result from an increased selectivity for the production of ethylbenzene over styrene. Using a favorable entropic effect, switching the supporting ligand from 4,4'-di-tert-butyl-2,2'-bipyridyl to 2,2'-dipyridylmethane (dpm) results in an increase in both catalyst longevity (by a factor of > 5) and activity (by a factor of ~2). In unpublished work, we have designed a new d8 catalyst that is highly selective for the synthesis of styrene from benzene and ethylene. This process is quantitatively selective for styrene and uses an oxidant that can be recycled using oxygen. For octahedral Ru(II) catalysts, building on previous structure/activity relationships, we successfully realized the prediction that cationic variants of TpRu(L)(NCMe)Ph (Tp = hydridotris(pyrazolyl)borate) catalysts should provide more effective catalysts for ethylene hydrophenylation. Reaction of the cationic Ru(II) complex [(HC(pz⁵)₃)Ru(P(OCH₂)₃CEt)(NCMe)Ph][BAR'₄] [HC(pz⁵)₃ = tris(5-methyl-pyrazolyl)methane; BAR'₄ = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate] (0.025 mol% relative to benzene) in benzene with C₂H₄

(15 psi) at 90°C gives 565 turnover numbers of ethylbenzene. The production of 565 turnovers of ethylbenzene corresponds to an approximate one-pass 95% yield with ethylene as the limiting reagent and is a 28-fold improvement compared to the charge neutral catalyst $\text{TpRu}(\text{P}(\text{OCH}_2)_3\text{CEt})(\text{NCMe})\text{Ph}$. In combination, the new cationic Ru(II) catalyst, the dpm-Pt(II) catalyst, and the new catalyst for styrene production are among the most effective for this class of catalyst for the production of alkyl and vinyl arenes using hydrocarbons.

Structured Carbon and Carbon-Oxide Composites as Catalysts and Catalyst Supports

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Funding: \$160,000 (2014)

PROGRAM SCOPE

Multi-walled carbon nanotubes (MWCNT) is a form of carbon that has two properties not shared by other carbon materials—it can have high surface area but with mesoporosity, rather than the microporosity of activated carbon, and be synthesized with good purity. It also has a hydrophobic surface which may be a disadvantage in aqueous media (making it difficult to disperse) and unreactive toward anchoring the catalytic active component (metal or oxide) to the MWCNT support. To provide anchoring sites and adjust the hydrophobicity, the surface can be functionalized by oxygen, usually accomplished by oxidation with nitric acid. The overall goal is to develop the fundamental catalytic science of MWCNT as structured carbon supports for reactions in aqueous media, with particular emphasis on reactions relevant to biomass processing. Two kinds of catalytic functions are desired: acid and hydrogenation. Acid catalysis is useful for aqueous hydrolysis, dehydration and alkylation and hydrogenation is often required to lower the O/C ratio, e.g., convert acids to alcohols in aqueous media. The two functions may be used in tandem, e.g., hydrolysis/hydrogenation of cellulose. Zirconium oxide may be a particularly flexible oxide for aqueous phase reactions because it can be both a support for metals and/or a strong acid catalyst when sulfated or tungstated. Thus, the zirconia/MWCNT composite suggests itself as a versatile platform for both acid and metal catalyzed reactions in hot water, or as a support for bifunctional catalysis by a metal particle in intimate association with a solid acid. The initial focus was on the synthesis and characterization of sulfated zirconia/MWCNT, followed by a comparison study of the synthesis and characterization of tungstated zirconia/MWCNT with respect to their relative aqueous stabilities and solid acid activities. These solid acids are to be converted to bifunctional catalysts by addition of a group VIII metal.

FY 2014 HIGHLIGHTS

The goal for $\text{ZrO}_2/\text{MWCNT}$ was to develop a hydrothermally stable support platform for a solid acid catalyst and we chose as our first example sulfated zirconia ($\text{S-ZrO}_2/\text{MWCNT}$) that has been well studied on bulk ZrO_2 . We have performed a combined Zr and S XANES analysis of $\text{S-ZrO}_2/\text{MWCNT}$ at the Zr LIII-edges and the S K-edge. A careful analysis of the S K-edge peak shape in the first and third derivative shows that the peak shape does not vary substantially at different treatment times at 450°C or after annealing at 550°C, well above the synthesis temperature, even though the S/Zr ratio decreases with both time at 450°C and temperature above 450°C. This would appear to rule out two different S species

unless they also had identical thermal stability. We propose instead that this peak be interpreted as one species with a two components; it can be compared to the two components of KHSO_4 . The spectrum of solid KHSO_4 maps onto the spectrum we observe for S-ZrO₂/MWCNT, while the spectrum of K_2SO_4 is identical to $(\text{NH}_4)_2\text{SO}_4$. On this basis we propose that the Brønsted site on S-ZrO₂/MWCNT is comprised of HSO_4^- anion interacting with a surface Zr cation (C. Liu *et al.*, *Top Catal.* (2014) 57, 696-705). Interaction between S and Zr already exists after impregnation but this interaction increases with a 250°C annealing because partial decomposition of $(\text{NH}_4)_2\text{SO}_4$ occurs, as detected by in-situ wide angle X-ray scattering, resulting in di-sulfur intermediate species, that more effectively accommodates and distributes the transferred charge than does the sulfur monomer. The picture that develops for S-ZrO₂/MWCNT acid sites is one where the Zr^{4+} cation plays a more passive role than usually attributed to it, but explains the perturbation of HSO_4^- by Zr interaction that results in a stronger acid, in terms of charge transfer (C. Liu *et al.*, *Top. Catal.* (2014) 57, 774-784).

Investigation of the Origin of Catalytic Activity in Oxide-Supported Nanoparticle Gold

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Funding: \$165,000 (2014)

PROGRAM SCOPE

Gold (Au) nanoparticles supported on reducible oxides such as TiO₂ demonstrate exceptional catalytic activity for a wide range of gas phase oxidation reactions such as CO oxidation, olefin epoxidation, and water gas shift catalysis. Scientists have recently shifted their hypotheses on the origin of the reactivity of these materials from the unique electronic properties and under-coordinated Au sites on nanometer-sized particles towards bifunctional sites at the Au-support interface. In 2011, we discovered a dual catalytic site at the perimeter of ~3 nm diameter Au particles supported on TiO₂ is responsible for oxidative catalytic activity. O₂ molecules bind with Au atoms and Ti⁴⁺ ions in the TiO₂ support and the weakened O-O bond dissociates at low temperatures proceeding to produce O atoms which act as oxidizing agents for molecules such as CO. Our DOE research has built on this finding and has been concerned with two aspects of the behavior of Au/TiO₂ catalysts: (1) Mechanistic behavior of dual catalytic sites in the oxidation of organic molecules such as ethylene and acetic acid; (2) Studies of the electronic properties of the TiO₂ (110) single crystal in relation to its participation in charge transfer at the occupied dual catalytic site. The research combines IR spectroscopic investigations of Au/TiO₂ catalysts with surface science on the TiO₂(110) surface and with modern density functional modeling. The goals of the work underway are to investigate the behavior of the dual Au/Ti⁴⁺ site for the partial oxidation of alcohols to acids, the hydrogenation of aldehydes and ketones to alcohols, and the condensation of oxygenate intermediates - all processes related to the utilization of biomass in the production of useful chemical energy sources.

FY 2014 HIGHLIGHTS

Our recent experimental and theoretical results provide insights into the active sites and pathways that control oxidation over Au/TiO₂ catalysts. Transmission infrared (IR) spectroscopic data show the direct involvement of the Au-Ti⁴⁺ dual perimeter sites, and density functional theory results connect the

electronic properties at these sites to their reactivity and to plausible reaction mechanisms. We also show the importance of interfacial Au-Ti⁴⁺ sites in adsorbing and activating O₂ as a result of charge transfer from the Au into antibonding states on O₂ causing di-σ interactions with interfacial Au-Ti⁴⁺ sites. This results in apparent activation energies for O₂ activation of 0.16-0.60 eV thus allowing these materials to operate over a wide range of temperatures (110-420 K) and offering the ability also to control H-H, and C-O bond scission. At low temperatures (100-130 K), adsorbed O₂ directly reacts with co-adsorbed CO or H₂. At higher temperatures, O₂ directly dissociates to form active oxygen adatoms (O*) on Au and TiO₂. These readily react with bound hydrocarbon intermediates via base-catalyzed nucleophilic attack on unsaturated C=O and C=C bonds or via activation of weakly acidic C-H or O-H bonds. The oxidative-dehydrogenation of model C₂-C₄ (acetic, propionic and butyric) carboxylic acids on Au/TiO₂ catalysts comprised of Au particles ~3 nm in size was investigated using IR spectroscopy and density functional theory. All three acids readily deprotonate to form their carboxylate analogs on the TiO₂ support which subsequently react to form a gold ketenylidene, Au₂C=C=O, intermediate along the way to their full oxidation. The adsorbed Au₂C=C=O intermediate species can be hydrogenated to produce ketene H₂C=C=O_(g), with an activation energy of 0.21 ± 0.05 eV. These studies show that selective oxidative-dehydrogenation of the alkyl side chains of fatty acids can be catalyzed by nanoparticle Au/TiO₂ at temperatures near 400 K.

Theoretical Investigation of Heterogeneous Catalysis at the Solid-Liquid Interface for the Conversion of Lignocellulosic Biomass Model Molecules

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Funding: \$380,000 (2014-2016)

PROGRAM SCOPE

The overall research goal of this project is the development and validation of a hierarchy of multi-scale methods for computing activation and reaction free energies of elementary processes occurring at metal-liquid interfaces that are only up to two orders of magnitude slower than current conventional catalysis tools for catalytic gas-solid studies. As a result, these novel tools will permit within a decade computational metal catalysis studies at solid-liquid interfaces with similar ease to current gas-metal catalysis studies (assuming a similar growth in computing infrastructure as seen in the past couple of decades). Our hierarchy of novel multi-scale methods starts with (i) the use of implicit solvation models to approximately describe solvation effects on elementary reactions at metal surfaces, (ii) the application of our hybrid quantum mechanics (QM) and molecular mechanics (MM) solvation scheme for computing free energies of reactions at metal-liquid interfaces, and (iii) the inclusion of solvent coordinates in the reaction coordinate when computing free energies with our QM/MM approach. As model systems for our computational study, we investigate selectivity issues in the reductive deoxygenation of ethylene glycol, glycerol, and guaiacol over metal catalysts under aqueous-phase processing (APP) conditions. Of key interest in these studies is understanding the specific effect of the liquid phase on the reaction mechanism and selectivity descriptors for future catalyst design studies.

FY 2014 HIGHLIGHTS

Within fiscal year 2014, we have applied our novel implicit solvation model for metal surfaces (iSMS) methodology to investigate the effects of various liquid solvents on the hydrodeoxygenation of propanoic acid over a Pd(111) model surface and on reforming reactions of ethylene glycol over a Pt(111) model surface. We observed that polar solvents such as water accelerate both the decarbonylation and decarboxylation rate of organic acid. Particularly, the decarboxylation that involves the formation of a charged carboxylate species is accelerated by two orders of magnitude. Next, an aqueous-phase microkinetic model predicts a 0.4 eV lower apparent activation energy in liquid water versus gas phase for reforming of ethylene glycol. Particularly at lower temperatures does liquid water accelerate reforming reactions. We also investigated the hydrodeoxygenation of guaiacol over Pt and Ru model surfaces. While over Ru catalysts decarbonylation reactions and C-OH bond cleavage can occur, leading to the formation of phenol, we find that over Pt catalysts catechol is the main reaction product and deoxygenation occurs only after hydrogenation of the phenyl group. As a result, it is challenging to produce oxygenated, aromatic products over Pt catalysts. Finally, we developed a hybrid quantum mechanics/molecular mechanics solvation scheme for computing free energies of reactions at metal-water interfaces. This explicit solvation model for metal surfaces (eSMS) is the first practical computational methodology for considering solvation effects in heterogeneous catalysis that uses explicit water molecules and permits extensive sampling of liquid water. Importantly, we find that both the iSMS and eSMS methodologies predict similar solvent effects for C-C bond cleavage of ethylene glycol over Pt(111).

Directed Surfaces Structures and Interfaces for Enhanced Electrocatalyst Activity, Selectivity, and Stability for Energy Conversion Reactions

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Funding: \$150,000 (2014)

PROGRAM SCOPE

The overarching goal of the project is to tune the activity, selectivity, and stability of catalysts for key electrochemical energy conversion reactions. We aim to accomplish this goal by designing and tailoring the surface structure and interfacial properties of catalyst materials at the nano- and atomic-scale. These goals project are directly in-line with the Grand Challenge in Catalysis Science as described in the DOE's 'Basic Needs Report for Catalysis in Energy': to design and synthesize catalyst materials with geometric and electronic structures tailored for high catalytic activity, stability, and selectivity. This project

FY 2014 HIGHLIGHTS

Two highlights to report involve catalyst development for the hydrogen evolution reaction (HER) and the oxygen reduction reaction (ORR). For the hydrogen-evolution reaction (HER), it is known with MoS₂ that only edge sites turnover the reaction because the basal planes are catalytically inert. In an effort to develop a scalable HER catalyst with an increased number of active sites, we synthesized thiomolybdate

$[\text{Mo}_3\text{S}_{13}]^{2-}$ nanoclusters in which most sulfur atoms in the structure exhibit a structural motif similar to that observed at MoS_2 edges. Indeed the supported $[\text{Mo}_3\text{S}_{13}]^{2-}$ nanoclusters exhibited excellent HER activity and stability in acid. Imaging at the atomic scale with scanning tunneling microscopy allowed for direct characterization and measurement of turnover frequencies (TOFs), shown to be higher than those observed for other non-precious metal catalysts synthesized by a scalable route. For details, see: J. Kibsgaard et. al., *Angewandte Chemie*, Vol. 6 (2014) 248-253. For the oxygen reduction reaction (ORR), we tuned binding energies of oxygen-containing intermediates on a catalyst surface by a strategy in which we can weaken the binding energies by means of thin-film overlayers, and strengthen them through nanoscale effects. By engineering a core-shell nanoparticle morphology with the appropriate dimensions, we showed that bonding properties can be modified to improve the catalytic activity of the core-shell system. We demonstrate the application of this strategy for oxygen reduction by identifying Ru@Pt as a candidate core-shell material using density functional theory calculations, and then use these calculations to guide the synthesis of active Ru@Pt core-shell catalysts. The Ru@Pt particles, synthesized using a wet chemical method, exhibit ~2 times higher specific activity (based on electrochemical active surface area) than state-of-the-art Pt/C from TKK. For details, see: A. Jackson et. al., *ChemElectroChem*, Vol. 1 (2014) 67-71

Atomically Precise Metal Nanoclusters for Catalytic Application

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PROGRAM SCOPE

We are motivated to create atomically precise metal nanoclusters (e.g. gold and bimetallic ones) for catalytic application. We have successfully attained thermodynamically stable gold nanoclusters protected by thiolates, such as $\text{Au}_{18}(\text{SR})_{14}$, $\text{Au}_{20}(\text{SR})_{16}$, $\text{Au}_{25}(\text{SR})_{18}$, $\text{Au}_{36}(\text{SR})_{24}$, $\text{Au}_{38}(\text{SR})_{24}$, $\text{Au}_{64}(\text{SR})_{32}$, $\text{Au}_{99}(\text{SR})_{42}$, and $\text{Au}_{144}(\text{SR})_{60}$. The atomic structures of nanoclusters are revealed by X-ray crystallographically. Our target is to achieve structure-catalytic reactivity correlation and fundamental understanding of some important issues of nanocatalysis, such as the precise size effect and the identification of catalytically active centers. Our research matches the research objective of the BES mission “to support fundamental research to understand, predict, and ultimately control matter and energy at the level of electrons, atoms, and molecules.

FY 2014 HIGHLIGHTS

The central goal of our project is to explore the catalytic application of atomically precise gold and gold-based bimetallic nanoclusters. We have successfully prepared different sized, robust gold nanoclusters protected by thiolates, such as $\text{Au}_{25}(\text{SR})_{18}$, $\text{Au}_{28}(\text{SR})_{20}$, $\text{Au}_{38}(\text{SR})_{24}$, $\text{Au}_{99}(\text{SR})_{42}$, $\text{Au}_{144}(\text{SR})_{60}$, etc. These ultrasmall nanoclusters (< 2 nm diameter) exhibit discrete electronic structures due to quantum size effects, as opposed to quasi-continuous band structure of conventional metal nanoparticles. We are particularly interested in investigating the unique catalytic properties of nanoclusters and aim to reveal the structure-selectivity relationships. Highlights of our year 2 work include: 1) C-H bond activation on nanoclusters (work reported in *J. Catal.*); 2) Chemoselective hydrogenation of nitrobenzaldehyde and

derivatives in water with H₂ (work published in J. Am. Chem. Soc.); 3) O₂ activation: singlet 1O₂ generation by visible light photoexcitation of Au₂₅(SR)₁₈ nanoclusters (work published in Chem. Mater. & J. Phys. Chem. Lett.); 4) Nanocluster structures (published in J. Am. Chem. Soc. and Nanoscale); 5) Size dependence in chemoselective hydrogenation and ligand effect in semihydrogenation (published in ACS Catal.). We have indeed identified some unique catalytic properties of nanoclusters not manifested in conventional nanogold catalysts; for examples, i) using Au₂₅ nanocluster catalysts we obtained ~100% yield in semihydrogenation of alkynes to alkenes, and ii) using thermally robust Au₉₉ nanocluster catalyst we obtained ~100% selectivity (or ~93% yield) in chemoselective hydrogenation of the aldehyde group in nitrobenzaldehyde to nitrobenzyl alcohol. These unique properties are not observed in conventional nanogold catalysts and are remarkable. The available atomic structures of nanoclusters (metal core plus surface ligands) serve as the basis for structure-property correlations and have revealed the molecular adsorption/activation sites.

Developing the Science of Immobilized Molecular Catalysts

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Funding: \$700,000 (2014)

PROGRAM SCOPE

A team of experimental and computational researchers from multiple universities are collaborating to investigate supported molecular catalysts. Cooperative catalysis, whereby two or more active sites work in concert in promoting a catalytic reaction, is ubiquitous in biological systems. Design and understanding of synthetic cooperative catalysts is the scientific target of this small team program. Past and current work has focused on the utilization of different cooperative M-Salen catalysts (where M has been Co or Al), whereby two M-Salen catalysts work together in the rate-limiting step to catalyze the reaction. An interdisciplinary research team that can probe all aspects of catalyst synthesis, structure and properties is exploring this topic from both experimental and theoretical points of view. In particular, researchers at GT and NYU are developing design principles for supported M-Salen catalysts that follow bimetallic (Co- and Al-Salen) reaction pathways, chiefly a family of Co-Salen catalyzed epoxide ring-opening reactions. Increasingly, other cooperative catalytic systems are being considered, including those that utilize organic active sites combining Brønsted acids and Lewis bases. Using these model systems, the fundamental principles that can be used to understand and design future classes of supported, cooperative catalysts are being elucidated.

FY 2014 HIGHLIGHTS

- 1) Heteroatom-substituted aminosilica catalysts were developed to investigate acid-base cooperative catalysis. Tuning of the metal-based active sites could yield improved activity associated with adjacent, tethered basic amine sites.
- 2) Trianionic ligands were designed to make Co(III) complexes for alcohol ring-opening of epoxides in an attempt to avoid counter-ion loss during reaction of the catalyst. These materials were found to

be catalytically inert under the conditions studied. Computational characterization of the electronic structure shows that Co(III) complexes with trianionic ligands do not have sufficient Lewis acidity to activate the epoxide.

- 3) Electronic structure computations were performed on the proposed rate-determining step of hydrolytic kinetic resolution of epoxides as catalyzed by Co(III)-Salen complexes. This work explains the inactivity of Co-Salen-OH when it is the sole catalytic species present (it arises from a higher barrier height, not an inability to activate epoxide).
- 4) Shell-crosslinked micelles and multicompartiment nanoreactors were developed as catalyst supports in cascade reactions. The catalytic transformations that have been investigated are hydrolytic kinetic resolution (HKR), epoxidation, and asymmetric transfer hydrogenation using Co, Mn, Ru and/or Rh-based transition metal catalysts.
- 5) Poly(2-oxazoline) block copolymer based micelle nanoreactors were investigated using density functional theory and molecular dynamics simulation. Flory-Huggins Chi-parameters were calculated to assess the miscibility of the POX homopolymers with various reactants and products. The correlation of this Chi-parameter to the experimental reaction data provided from other team members suggested that the higher the miscibility of reactant in the phase of the corona polymer, the faster the reaction completion, which indicates that the transport of reactant and are determined by the molecular interactions with the micelles.

Transition Metal Activation & Functionalization of Carbon-Hydrogen Carbon-Carbon Bonds

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

This project is directed towards fundamental investigations of the reactions of homogeneous transition metal complexes with aliphatic and aromatic hydrocarbons, saturated and unsaturated, and their functionalized derivatives (e.g. carbonyl, nitrile, halides). The studies provide fundamental information about the mechanisms and energetics of reactions of metal complexes with C–H, C–C, and C–X bonds in a wide variety of hydrocarbons. The key to understanding reactivity of these molecules lies in determination of the kinetic and thermodynamic selectivity for cleavage of these bonds by coordinatively unsaturated metal species. Determination of metal-carbon bond strengths is critical to understanding the thermodynamic factors that control the reactions. New ways to determine these bond strengths with a variety of substrates and new metal complexes will be explored. The work will be extended to include determination of metal-alkoxide bond strengths. New substrates for the cleavage of C–C bonds will be sought extending the examples that include sp , sp^2 , and sp^3 hybridized carbon. New metal complexes for cleaving these bonds will be found. The interplay between η^2 -coordination, C–H oxidative addition, and C–C oxidative addition will be applied to the cleavage of C–C linkages. We will examine in detail how Lewis acids can affect the kinetics and thermodynamics of C–C activation. In all of these areas, we will apply DFT theory to examine stabilities of reactants, intermediates, and transition states, providing a comprehensive understanding of strong bond activation. The success of this work will lead to new approaches for the manipulation of petroleum-based hydrocarbons and functionalized

derivatives. New processes for making and breaking strong bonds in organic molecules will be based upon the lessons learned from the kinetic and thermodynamic studies of the type presented here.

FY 2014 HIGHLIGHTS

The most important discoveries in C–H activation that have been made in this project include: (1) We have made a breakthrough in understanding factors that influence metal-carbon bond strengths by examination of the activation of CH₃CN by [Tp'Rh(CNR)] and comparing this to methane activation. Tp'Rh(CNR)(CH₂CN)H loses CH₃CN with a half-life of 3 days at 100°C, whereas Tp'Rh(CNR)(CH₃)H loses CH₄ with a half-life of 5 hours at 25°C, suggesting that the effect of an alpha-cyano substituent strengthens the metal-carbon bond. However, our kinetic methodology shows that the Rh–CH₂CN bond is actually 3 kcal/mol weaker than the Rh–CH₃ bond! This result shouldn't be so surprising considering the organic radicals that are formed (unstable ·CH₃ vs. stable ·CH₂CN). The greater apparent stability of the oxidative addition product arises because reductive elimination produces a wimpy H–CH₂CN bond (95 kcal/mol) whereas methane elimination produces a hefty H–CH₃ bond (105 kcal/mol). Hence the apparent 'stability' is associated with a weaker M–C bond! (2) We have extended this analysis to include a wide range of substituted methyl derivatives of the type Tp'(CNR)(H)Rh–CH₂X where CH₂X = CH₂Cl, CH₂OMe, CH₂OtBu, CH₂C(=O)CH₃, CH₂C≡CCH₃, CH₂aryl, CH₂CMe=CH₂, CH₂F, CHF₂ and CH₂CF₃. These substrates all show a linear correlation of D(Rh–C) vs. D(C–H) that is parallel to the line for the parent hydrocarbons, but displaced by ~7 kcal/mol higher in energy. This shift is attributed to the greater ionic contribution to the Rh–C bond in these derivatives. (3) This same trend has been investigated in Tp'(PMe₃)(H)Rh–CH₂X derivatives, and the same trends are seen separating the parent hydrocarbons from the substituted methyl derivatives. The difference here is that the slope is greater for the PMe₃ complexes. (4) The trend was also observed in a series of Tp'(P(OMe)₃)(H)Rh–CH₂X derivatives, but the slope of the trend was in between that seen with CNR and PMe₃ spectator ligands.

Control of Supported Molecular Catalysts Using Metallocalixarene Active Sites

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Funding: \$400,000 (2014-2016)

PROGRAM SCOPE

Molecular engineering of catalysts on surfaces has resulted in unique compositions that control the local density of grafted cations on surfaces (demonstrated on silica) as well as control of Lewis-acid catalysis via coordination geometry surrounding grafted metal cation on surface (also demonstrated on silica). In the first area, more robust grafted Ti center catalysts have been synthesized, which withstand the harshness of protic solvents and do not leach. In the second area, unique demonstration of coordination geometry linking to catalytic activity is made using organic ligands grafted on surfaces.

FY 2014 HIGHLIGHTS

We have synthesized a unique example of patterned grafted cations on surfaces, by tethering Ti(IV)-metallocalixarene complexes to an aromatic core. We have also demonstrated the resulting materials to

be more robust against leaching compared with the randomly distributed isolated grafted metallocalixarenes, which is attributed to encapsulation within mesopores of silica. Catalysis was used to demonstrate the grafting of all four calixarenes within a molecule to the silica surface, since this grafting makes the metallocalixarene complex an active catalyst for olefin epoxidation, compared to the lack of activity prior to grafting. We have also synthesized unique catalysts for the transformation of aldehydes to esters via Tishchenko reaction, using grafted Al(III)-calixarenes. This emerging area nicely connects homogeneous and heterogeneous catalysis, since alkoxides of Al have been long used as soluble catalysts for this reaction. Our results show that Al within an O environment enforced by a grafted calixarene and the silica surface is an active solid catalyst for the Tishchenko reaction. Preliminary data points to a pronounced effect of calixarene coordination and geometry on the catalyst activity.

Direct Epoxidations Using Molecular Oxygen

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Funding: \$200,000 (2014)

PROGRAM SCOPE

Our work continues in the area of using homogeneous and to a more limited extent Cu-based heterogeneous catalysts with molecular oxygen to broadly examine oxygen transfer reactions to both organic and inorganic substrates to yield valuable, partially oxidized products. The oxidation reactions of primary interest to us are those that have no counterparts (either heterogeneous or homogeneous) when using gaseous O₂. Our homogeneous catalytic approach is centered upon the use of pincer-ligated late transition metal hydrides as the starting complex, which then adds O₂ to form reactive metal hydroperoxides. We have shown that these M-OOH species are stable enough in general to be fully characterized; yet reactive enough to transfer oxygen in certain cases to give oxidized products and a metal hydroxide complex. Addition of hydrogen to the M-OH species regenerates the starting hydride, along with water. Much of our work is directed towards preparing new complexes for evaluation, along with understanding these fundamental steps in the proposed catalytic cycle. While developing useful and efficient routes to these oxygenated organic compounds is the primary goal for our work, we are also interested in understanding the fundamental mechanistic chemistry of oxygen insertion and transfer using transition metal complexes. The understanding generated in our work should be applicable to other systems of interest to DOE, thus increasing the reach and impact of our fundamental studies. As this is a highly-collaborative project among our teams and outside collaborators, a highly communicative and integrated research effort between UNM and UW is required to accomplish these goals.

FY 2014 HIGHLIGHTS

We have prepared and characterized multiple new late transition metal pincer systems and investigated their ability to perform specific chemical transformations proposed in an olefin epoxidation sequence using molecular oxygen. Phosphine based PNP pincer systems of palladium and platinum capable of metal-ligand cooperativity were extensively studied. This work provided key insight into the

requirements of the ligand and metal center for O₂ reactivity with M-H bonds. The results were published in *Organometallics*. This past year, we also began a collaboration with Dr. Giuliano Giambastiani at the Institute of Chemistry of OrganoMetallic Compounds ICCOM-CNR in Florence, Italy. Palladium complexes bearing novel asymmetric PCN pincer ligands were prepared by their group and subsequently investigated by us. A variety of palladium hydroxide mononuclear and dinuclear complexes were synthesized, characterized and their reactivity with H₂ was investigated. A manuscript is in preparation. Finally, after further analysis of the requirements for the complete epoxidation cycle, promising new ligands have been identified and targeted. Inspired by the mechanism of organic peracid epoxidation, the bifunctional ligands will assist in both the activation of oxygen as well as the substrate oxidation step. In addition to journal articles, the work described above will also be incorporated into a PhD thesis at UW. We are also working on demonstrating the transfer chemistry of oxygen into inorganic substrates, in particular into the Si-H bond to form valuable Si-OH species. While O transfer is clearly occurring, the selectivities to unique products appear to be highly substrate-dependent. We anticipate understanding the structural features affecting selectivity in early 2015. As well, the heterogeneous work that has led to production of propylene oxide using Cu-based catalysts has been completed, and will be a key part of a PhD thesis at UNM.

Catalysis, Dynamics and Stability of Enzymes under Extreme Conditions

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Funding: \$160,000 (2014)

PROGRAM SCOPE

Biocatalysis offers attractive new alternatives to chemical catalysis and transformations. The power of enzyme-catalyzed chemical transformations for the production of molecules that require complicated chemistry, stereochemistry, selectivity and at the same time satisfy environmental constraints has been widely recognized. However, while a large range of physical conditions can be used for chemical reactions, a major challenge of biocatalysis is that enzymes usually function in aqueous solutions at ambient temperature, pressure, low ionic strengths and pH values around neutral. While these properties have historically restricted the applications of biocatalysts, the discovery of organisms that live under extreme conditions (called extremophiles) opens a new era for biotransformations.

- Since extremozymes are stable and active under these extreme conditions, they are attractive as biocatalysts to industries such as chemical synthesis, agriculture, laundry detergents and the pharmaceutical industry. Enzymes from extremophiles can be exploited either by using them directly or by using the knowledge of how they adapt to extreme conditions to modify mesophilic proteins accordingly.
- We utilize the unique properties of extremophiles to study protein structure, dynamics and catalysis under a wide range of conditions. The long-term goal is to identify basic physical principles of protein stability and dynamics and their linkage to enzymatic activity for future use in rational design of biocatalysts. The lack of understanding of protein dynamics is most likely the reason for the limited success of designing biocatalysts. This research proposal is aiming to provide such information.

FY 2014 HIGHLIGHTS

We have characterized at atomic resolution all the microscopic steps in the catalytic cycle of adenylate kinase, through a combination of NMR measurements during catalysis, pre-steady-state kinetics, MD simulations, and crystallography of active complexes. Surprisingly we found that the Mg^{2+} cofactor activates two distinct molecular events, phosphoryl transfer (>105-fold) and lid-opening (103-fold). Our results highlight the importance of the entire energy landscape in enzyme catalysis and suggest that adenylate kinases have evolved to catalyze key processes simultaneously by precise placement of a single, charged and very abundant cofactor in the active site. •We have investigated the detailed mechanism by which Adk accelerates the P-transfer step by more than 8 orders of magnitude. From the QM calculations we got profound insights that may be a crucial reason for why enzymes are better catalysts than simple catalysts: The transition state is not a single state but rather a collection of structurally quite different states. The “broad” nature of the transition state for the enzyme-catalyzed reaction might be an important feature for efficient lowering of the barrier. •We started investigating the evolution of enzymes 4 billion years back from the last common ancestor between modern thermophilic, mesophilic and psychrophilic Adk. First we measured the thermostability of all enzymes. The oldest ancestor is very thermostable. Thermostability decreases along the evolutionary branches to the psychrophile and mesophile, and re-evolves thermostability in the lineage to the modern thermophile. Even more exciting are the results about the evolution of enzymatic activity. Wolfenden and coworkers hypothesized that in evolution, chemical reactions that were possible in hot environments got too slow when the earth cooled down. In order for these reactions to proceed at these lower temperatures, nature evolved enzymes with a large decrease of the free enthalpy of activation.

EARLY CAREER: Multifunctional Oxygen Evolution Electrocatalyst Design and Synthesis

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Funding: \$150,000 (2014)

PROGRAM SCOPE

In this project we aim to develop new multicomponent oxide-based electrocatalysts for the oxygen evolution reaction using combined theoretical and experimental approaches. We use density functional theory to compute the electronic structure and reactivity proxies of model oxide materials. From the understanding generated from these calculations, we synthesize materials and characterize their oxygen evolution activity. We use *in situ* spectroscopic methods to characterize oxide electrodes under reaction conditions. We also develop new data sharing strategies to facilitate the reuse of our data by others.

FY 2014 HIGHLIGHTS

- Development of the jmax scientific publishing software suite. All of our papers have been written with this open-source tool.

- Obtained unambiguous evidence of an electrolyte promotion effect for Ni oxide-based electrocatalysts
- Found new descriptors for oxide reactivity using density functional theory

Molecular Engineering for Selective Catalysis

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 Funding: \$100,000 (2014)

PROGRAM SCOPE

The unique properties stem from the constrained environment and enforced proximity of functional groups in a molecular-size cavity have given rise to very interesting material properties, most remarkably catalysis by enzymes. The goal of this project is to investigate such nanoconfinement effects in abiotic systems and understand the relevant chemical interactions, so as to enable design of catalytic structures of targeted properties. The approach is to synthesize structures with defined environment around an active site and explore how the environment influences the properties of the functional groups and metal complexes within. The experimental plan was to design, synthesize, and characterize structures of siloxane and carbosilane-based material and graphene oxide to explore the nanoconfinement effects. The first system is a core-shell bifunctional nanocage, which has been synthesized successfully by us recently. Preliminary results suggested that it could stabilize a monocarbonyl Co(I) complex formed by reaction of cobalt carbonyl with interior carboxylic acid groups. This complex has an uncommon oxidation state and ligand combination. This project will explore the formation, structural, chemical and catalytic properties of metal complexes in the nanocage derived from reaction of carbonyls of Co, Fe, and Ni. The effect of stability of metal oxidation states will be examined, together with their catalytic hydrogenation and oxidation capability. Other complexes of Pt and Au will be generated inside the core-shell nanocage, and the effect of forced binding to “hard” ligands on their catalytic properties will be examined. These complexes will be compared with complexes of Pd that binds more strongly with the interior functional groups. The second system is to explore a new class of nanocavity made from modified “holey” graphene oxide sheets.

FY 2014 HIGHLIGHTS

Discrete nanocages of a core-shell structure, in which the core possesses periphery carboxylic acids and the shell interior silanols, reacted with cobalt carbonyl to form a monocarbonyl Co(I) complex. The formation and stabilization of this complex of an uncommon oxidation state of Co was because of steric crowding, such that the motion of the interior carboxylic acid groups was restricted, which led to a condition in which the cobalt carbonyl could only react with a limited number of carboxylic acid groups to form the Co(I) complex. Its formation inside the nanocage was concluded from various characterization measurements. Its stoichiometry of one CO ligand per Co(I) was determined by measuring the amount of CO released after decomposing the complex. The oxidation state was confirmed with EPR spectroscopy. The initially EPR inactive Co species was transformed to one that displayed an EPR signal at $g=4.0$ after exposure to molecular O₂. The IR stretching frequency of the single CO ligand at 1958 cm⁻¹ was also consistent with a Co(I) oxidation state. The location of the Co(I) inside

the nanocage was inferred from the lack of redox peaks in CV measurement, and from the fact that it could be oxidized readily by the smaller phenyl azide but not the larger adamantane azide due to steric hindrance by the porous shell. Another complex, POSS-Sn-POSS, was prepared in which the Sn cation possessed a tetrahedral symmetry with four siloxy ligand bonds. Its coordination symmetry was confirmed by the chemical shift in the ^{119}Sn NMR, EXAFS, and single crystal X-ray diffraction pattern. The Sn cation was a Lewis acid, and it coordinated diethylamine in an anti- configuration, whereas it bound ethylene diamine in a syn- configuration, both forming an octahedral complex. Interestingly, it only interacted with triethylamine weakly without noticeable change in the coordination symmetry at Sn.

Development of Physically Transparent, Predictive Structure-Performance Relationships for Rational Design of Multi-Component Catalytic Materials

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Funding: \$460,000 (2014-2016)

PROGRAM SCOPE

Metals are used as catalyst for many chemical transformations. These materials are usually heavily promoted with multiple additives which serve to further improve the rates and/or selectivity of the process. The central theme of the project is to study how perturbations of metal surfaces by chemical promotion (for example promotion by alkali adsorbates), poisoning, or alloying, affect their chemical and catalytic behavior. The ultimate objective is to develop simple, physically transparent, predictive models of chemisorption on these materials. To accomplish these objectives we utilize first-principles Density Functional Theory (DFT) calculations, ab-initio atomistic thermodynamics and kinetic simulations and a slate of experimental techniques to measure geometric and electronic structure of catalytic materials as well as their performance. We envision that these models can guide us in a rapid screening and discovery of efficient multi-component catalysts (e.g., alloys).

FY 2014 HIGHLIGHTS

- i. We have developed a very general and physically transparent framework, grounded in DFT calculations, to systematically study the effects of a perturbation of a metal surface on its chemical activity. This framework allows us to distinguish between various effects, including electrostatic, polarization, and electronic mechanisms. A fairly simple procedure was developed to evaluate independently the different contributions to the perturbation energy.
- ii. This model was utilized to probe the effects of alloying (or the formation of inter-metallic compounds) on the chemical activity of various sites in the alloy. Under these efforts we made the following observations: (a) Experimental measurements of the electronic structure of a number of Pt and Ni alloys along with DFT calculations were used to develop, verify, and validate simple predictive structure-property models relating the local geometric structure of alloy sites to their chemical activity (the strength of interaction with adsorbates). The fundamental advantage of the model is that the chemical activity is predicted based only on physical properties of elements that form the alloy in their unalloyed form, (b) The model was used to screen rapidly through a large alloy space seeking optimal alloy catalysts for a number of chemical reactions, including

electrochemical oxygen reduction reaction in acid and base leading us to the discovery of a few promising alloys for these important reactions.

- iii. We have synthesized and tested a number of Pt- and Ag-based alloys for ORR in acid and base respectively, demonstrated excellent performance of these electro-catalysts. Some of these alloys exhibited the performance that is potentially of commercial significance.

The Physical and Chemical Properties of Nanostructured Mixed-Metal Catalysts

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

Overall Research Goals and Specific Objectives for the period 1/1/14-12/31/14 The main targets of this study has been to synthesize well-defined nanoparticles of Pt and Ni as well as mixed-metal nanoparticles on different substrates, including ultrathin oxide surfaces, graphene moiré structure, and hexagonal boron nitride pore-wire structures (h-BN) grown on refractory metals. Graphene moiré structure and h-BN substrates provide periodic and identical nucleation sites for metal particle formation. The focus of the research is an understanding of the effects of metal-substrate interactions on the structure/stability of nanoparticles and the effects of particle size and overall surface composition on their catalytic activity. The reactions we focused on were light alkane dehydrogenations. DOE Interest and Potential Impact: New strategies for the synthesis of well-defined nanostructured catalysts that are highly stable toward reaction conditions and thermal-induced sintering are necessary for the development of highly dispersed, size-limited catalysts for new catalytic applications. The development of *in situ* methods for characterizing the morphology of nanocatalysts and the surface species formed during reaction are keys to the ultimate synthesis of practical commercial nanocatalysts. These key issues are central to the proposed work.

FY 2014 HIGHLIGHTS

1. 'Graphene cover-promoted metal-catalyzed reactions' PNAS 111 (2014) 17023-17028 (collaborative project). Institutional Contributions: Texas A&M University:TPD, PMIRAS, and reaction kinetics Dalian Institute of Chemical Physics:LEEM Lawrence Berkeley National Laboratory: High pressure XPS Rensselaer Polytechnic Institute: DFT simulation
2. Dehydrogenation of n-hexane over sub-nanometer Ni particles (manuscript submitted) Conversion of n-hexane in the presence of hydrogen was studied on a series of model Ni/SiO₂ catalysts having an average Ni particle size from 1.1 nm to 5.5 nm. The model catalysts were prepared by vapor depositing Ni onto a planar SiO₂ film. It was found that over small (< 2 nm) Ni particles the principal reaction that occurs during n-hexane conversion at 673K was dehydrocyclization to benzene, whereas over larger Ni particles hydrogenolysis to methane and ethane is the predominant reaction. The effects of reactant partial pressures on product distributions and on the formation of carbonaceous deposits were also studied.

Supported Organometallic Complexes: Surface Chemistry, Spectroscopy, Catalysis, and Homogeneous Models

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Funding: \$63,000 (2014)

PROGRAM SCOPE

Many important yet poorly understood catalytic reactions involve the creation and transformations of metal-hydrocarbyl, -hydride, -alkylidene/alkylidyne, and π -complexes on solid surfaces. An informative means to investigate these species and, by doing so, to create new or and/or improved homogeneous and heterogeneous catalysts, is via chemisorption and characterization, under controlled conditions, of structurally precise organometallic precursors on reactive surfaces having well-understood chemical and structural properties. For certain classes of metal hydrocarbyls, chemisorption on high surface area oxides is known to be accompanied by dramatic catalytic activity enhancements vs. their behavior in solution, and the origin of these effects is poorly understood. Under DOE support, we have explored catalytic processes at the homogeneous/heterogeneous interface, probing how (catalyst)-surface, (catalyst)-weakly interacting ligand group, and (catalyst)-catalyst interactions afford new, instructive, and useful reactivity. The focus on chemisorbed groups 4, 5, and f-element organometallics has moved from relatively simple oxides, to “super Brønsted acid” surfaces which create very electrophilic and reactive species in high densities (up to 100% active sites). Integrated product, *in situ/operando* spectroscopic, and mechanistic studies probe chemisorption pathways, adsorbate structures, catalytic reactions (scope, selectivity, kinetics, isotopic labeling, active site counting, etc.), and the energy storage properties of polyolefin/ferroelectric oxide composite materials prepared by this chemistry *in situ*. In parallel, homogeneous chemistry has focused on models for isolated and adjacent adsorbed species, moved to encompass group 10 metals, investigated the effects of weak interactions such as ion-pairing and proximate ligand substituents, (catalyst center)⁺(catalyst center) cooperative effects, and new catalytic transformations.

FY 2014 HIGHLIGHTS

The goal of this interdisciplinary homogeneous-heterogeneous catalytic research effort is to model, understand at a fundamental level, expand, and exploit the unique pathways by which organometallic molecules of varying nuclearity undergo chemisorptive activation and dramatic catalytic activity enhancement on solid surfaces. These processes connect to real-world, large-scale industrial hydrocarbon processes and to manufacturing cleaner, greener, more environmentally acceptable products, including those from sustainable resources. The research effort combines catalyst synthesis, surface chemistry and spectroscopy, homogeneous analogue catalysis, structural analysis, and computation, and involves collaboration with U.S. national laboratories and U.S. industry. Highlights over the past year included: 1) Investigated mononuclear and binuclear organometallic chemisorption on “super Brønsted acid” oxides, thereby elucidating their structures and the mechanisms by which these unusual, highly electrophilic species effect distinctive catalytic polymerization and hydrogenation processes, 2) Designed, synthesized, and characterized mononuclear and polynuclear catalyst precursors for the above chemisorption, and compared those catalytic properties to the same species in

homogeneous solution. Showed that adsorption on the super acid surfaces creates more electrophilic, less heavily ion-paired catalysts. 3) Computationally modeled both the chemisorbed catalysts and their reactivity/selectivity modalities, showing the importance of the surface in dispersing negative charge. Argued that the surfaces come very close to the “holy grail” of the ultimate non-coordinating anion. 4) Employed this information to design and catalytically produce new types of nanocomposite energy storage materials with very high charge storage capacity.

Atomic-Scale Design of Metal and Alloy Catalysts: A Combined Theoretical and Experimental Approach

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Funding: \$620,000 (2014-2016)

PROGRAM SCOPE

The first-principles design of heterogeneous catalysts can produce novel materials with significantly enhanced catalytic properties. Using state-of-the-art density functional theory (DFT) methods in conjunction with reactivity experiments and microkinetic modeling, we determine the detailed reaction mechanism of catalytic reactions of interest. By investigating these reactions over a series of monometallic surfaces, we elucidate reactivity trends which allow the identification of key reactivity descriptors. These descriptors are then utilized in the design of alloy catalysts that are predicted to have high activity and selectivity toward desired products. Because catalytic reactions are generally sensitive to the specific composition and geometric arrangement of atoms at and near the surface of the catalysts, these catalytic reactions can benefit tremendously by advanced inorganic synthesis methodologies delivering the theoretically predicted optimal nano-architecture of the catalytic nanoparticles. The novel catalysts synthesized with these methods are subsequently characterized and evaluated through a variety of state-of-the-art experimental methods.

FY 2014 HIGHLIGHTS

In a nutshell, our research combines quantum mechanical design at the atomic scale with advanced inorganic synthesis techniques to yield catalytic nanoparticles of controlled size and shape, characterized by improved activity and selectivity for targeted vapor phase and electrocatalytic reactions. We have made considerable progress toward our goals during this past year. In particular, we have made great strides in understanding fundamental aspects of: (1) complex metal/metal oxide interfaces, which are important for most heterogeneous catalysis in general, and in particular for the water gas shift reaction and the preferential oxidation of CO in hydrogen, (2) metal alloy catalysts, particularly for electrocatalytic reactions such as the oxygen reduction reaction (ORR) and methanol electro-oxidation, (3) new methods for the synthesis of size- and shape-selected monometallic and alloy nanocrystals as optimized catalysts.

Investigations of C-H Bond Activation and Doped Metal Oxide Catalysts

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Michael Gordon; California-Santa Barbara, University of
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Funding: \$580,000 (2014-2016)

PROGRAM SCOPE

The goals of our research are: to improve the catalytic performance of complex metal oxides by chemical modifications such as doping with different anions or cations; to achieve a more thorough understanding of the basic mechanisms of catalytic processes on doped oxide surfaces; to discover new catalysts for alkane conversion to more valuable chemicals; to develop a broad theory-based framework in which hydrocarbon reactions with these catalysts may be more generally understood. The aim is to find catalysts that can operate under the conditions present in industrial reactors and that might be economically competitive with the commercial catalysts.

FY 2014 HIGHLIGHTS

During the last year of work we have completed a number of theoretical and experimental studies. In trying to understand why molten lithium chloride supported on MgO is one of the best performing ethane oxidative dehydrogenation catalysts, we are able to rule out LiOCl, LiO₂ and Cl₂(g) as oxidative intermediates using ab-initio molecular dynamics. In studies of the reactivity of vanadium pentoxide (V₂O₅) as an oxidation catalyst, possible surface reconstructions have been overlooked, which artificially increase the chemical reactivity of the (100) and (001) surfaces. Using DFT we found reconstructions for both surfaces. Based on oxygen vacancy formation energies, we now estimate the reactivity of the surfaces to be much closer to the stable exfoliation (010) surface. We previously reported ruthenium doped ceria to be active for CO₂ methanation. Further work has given insight into the mechanism of the reaction. We have shown that CO₂ methanation takes place through surface carbonate intermediates and depends on the degree of reduction of the ruthenium-doped ceria catalyst. Two component systems of catalysts and metal oxide reactants were explored for producing propylene from propane (and generally any alkane dehydrogenation) in yields above those possible by thermal dehydrogenation alone. Platinum- or chromium- based catalysts and copper or bismuth based selective hydrogen combustion solid oxides were explored. These material systems are potential drop-in replacements for existing propane dehydrogenation infrastructure. In new experiments, we built a molten lithium iodide salt reactor system for propane oxidative dehydrogenation and achieved the highest reported propylene yields from propane for any ODH catalyst. The addition of bromine to the melt has profound influence and, in the gas phase, iodine appears to facilitate the conversion of HBr and oxygen to bromine and water.

Selectivity Control through Modification of Metal Catalysts with Organic Monolayers

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Students: 0 Postdoctoral Fellow(s), 4 Graduate(s), 1 Undergraduate(s)
Funding: \$170,000 (2014)

PROGRAM SCOPE

The overall goal of this work is to investigate the use of organic self-assembled monolayers as modifiers for supported metal and metal oxide catalysts. By tailoring the properties of the monolayer-forming species, one can control both the surface and near-surface environment to improve chemoselectivity in key reaction chemistries. A combination of catalyst screening experiments and surface vibrational spectroscopy is being used to understand mechanisms by which monolayers can influence catalyst activity and selectivity in several probe reactions.

FY 2014 HIGHLIGHTS

In recent work, we have shown that self-assembled monolayers can have at least three effects that profoundly influence catalytic activity and selectivity on late transition metal surfaces: (1) steric interactions, where the crowding by the monolayer allows only certain reactants or reactant conformations to reach the surface; (2) active site selection, where the monolayer blocks particular types of surface sites that are associated with undesired reactions; and (3) molecular recognition, in which interactions between the reactant and monolayer in the near-surface environment favor binding of the reactant in specific configurations. These mechanisms have been demonstrated for a number of key reaction chemistries, including hydrodeoxygenation of biomass-derived compounds, hydrogenation/isomerization of olefins, and hydrogenation of unsaturated aldehydes. Most recently, we have investigated factors that control monolayer stability, and have demonstrated strategies (such as cross-linking between monolayer ligands) that enhance the stability of organic films under reaction conditions.

Synthesis and Exploratory Catalysis of 3D Metals: Group-Transfer Reactions, and the Activation and Functionalization of Small Molecules Including Greenhouse Gases

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Funding: \$380,000 (2014-2016)

PROGRAM SCOPE

Our research program has developed synthetic entries to molecular examples of well-defined vanadium and titanium nitrides given their implications in important transformations such as the dehydrogenation of alkanes. We have found that deprotonation of the parent titanium imido (^{tBu}nacnac)Ti≡NH(NtolyI₂) (^{tBu}nacnac⁻ = [ArNC^tBu]₂CH; Ar = 2,6-iPr₂C₆H₃) with KCH₂Ph forms the molecular titanium nitride anion as a dimer, {[K][(^{tBu}nacnac)Ti≡N(NtolyI₂)]}₂. From the parent imido or nitride salt, the corresponding aluminylimido–etherate adduct, (^{tBu}nacnac)Ti≡N[AlMe₂(OEt₂)](NtolyI₂), can be isolated and structurally characterized. The parent imido is also a source for the related borylimido, (^{tBu}nacnac)Ti=NBt₂(NtolyI₂). Other reactivity of the nitride or parent titanium imide will be presented as well as new ligand scaffolds (such as a phosphine-anilide) that can potentially support the terminal nitride or nitridyl ligand on titanium.

FY 2014 HIGHLIGHTS

During this period our group discovered synthetic entries to molecular complexes of vanadium and titanium nitrides. We performed mechanistic studies to try and understand the process to formation of terminally bound vanadium nitrides. In addition the reactivity of the vanadium nitride ligand has been explored via one- and two-electron reductants whereby the nitrido ligand acts as a conduit for electron transfer. We have also discovered routes to the first examples of well-defined titanium nitrides (in the form of nitride anions), via deprotonation of a parent imido ligand bound to titanium. Salt elimination reactions have allowed us to prepared new ligand scaffolds on titanium, and we have presently found a direct route to titanium nitrides complexes supported by a robust phosphino-anilide ligand.

Surface Chemical Studies of Gold Model Catalysts

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Funding: \$150,000 (2014)

PROGRAM SCOPE

Gold nanoparticles have shown remarkable properties in catalyzing environmentally-important and industrially-relevant chemical reactions under relatively mild conditions. We are studying surface chemical reactions on model gold catalysts using ultrahigh vacuum surface science techniques as well as batch reactivity measurements at pressures between 1 and 100 Torr. We employ two major surface catalytic themes regarding the chemistry of these model gold surfaces that build on our experience from the recent past: (i) reactions of adsorbed hydrogen atoms with other relevant molecules on single crystalline gold samples in an ultrahigh vacuum environment and (ii) oxidation reactions on gold surfaces populated by nanoparticles of metal oxides (i.e., inverse model catalyst) at pressures between ~1-100 Torr in a batch reactor as well under ultrahigh vacuum conditions. We will physically characterize these model catalyst surfaces employing several surface sensitive tools. For chemical characterization, we will employ molecular beam surface scattering techniques, temperature programmed reaction spectroscopy, infra-red vibrational spectroscopy, density functional theory calculations (via a collaboration with Professor Graeme Henkelman), and higher pressure (1-100 Torr) batch catalytic measurements on our gold model catalyst surfaces. We will synthesize our inverse model gold catalyst surfaces employing a simple reactive physical vapor deposition technique on the Au(111) substrate. We expect that the proposed research will impact, more generally, the fundamental understanding of gold catalytic chemistry.

FY 2014 HIGHLIGHTS

We published six archival journal articles describing our experimental findings during this one year period. We also have created a new laboratory for conducting catalytic measurements on high surface area catalysts at atmospheric pressure via a flow reactor along with the necessary physical characterization measurements. This area of catalysis science is new to my group and the studies will complement the measurements that we make in ultrahigh vacuum employing single crystalline samples.

We are currently making measurements of vanadia supported gold catalyst for the water-gas shift reaction.

EARLY CAREER: Room Temperature Electrochemical Upgrading of Methane to Oxygenate Fuels

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Funding: \$160,000 (2014)

PROGRAM SCOPE

With recent discoveries of vast amounts of shale methane deposits in Pennsylvania and the Dakotas, and the introduction of renewable biogas to the market, the availability of methane in the United States is at an all-time high. High petroleum prices and an increased emphasis on domestic energy security will make methane-to-fuels (MTF) processes even more important in the near-future than they are today. Current MTF processes are initiated through the steam reforming of methane to syngas ($\text{CO} + \text{H}_2$), followed by catalytic re-reduction of CO by H_2 to hydrocarbon and oxygenate fuels. Unfortunately, steam reforming requires a combination of high temperature (900-1100°C) and large heat requirement, making the process expensive, placing severe stress on materials, necessitating complex heat integration schemes, leading to poor reaction selectivity, requiring expensive gas separation processes and emitting a significant amount of CO_2 . The objectives of this research are to understand the underlying mechanisms for the direct electrochemical conversion of methane to syngas at room temperature, and develop new electrocatalysts that convert methane to methanol at room temperature (T 90%) to overcome the limitations of existing MTF processes. Methanol was selected as the target molecule because it can be used directly as an energy source and it is the primary precursor for the manufacture of many commodity chemicals, making it one of the most produced and important industrial chemicals in the world. However, this project will have far reaching applications, providing a new pathway for the electrochemical synthesis of complex oxygenates and long-chain hydrocarbons through the formation of new C-O and C-C bonds.

FY 2014 HIGHLIGHTS

In the past fiscal year, our team has taken several important steps forward. In this past fiscal year, the team has shown that our system is able to synthesize all of the targeted oxygenates: methanol, formaldehyde, and CO. The team has also demonstrated that the oxygenate selectivity can be controlled with the operating voltage (anode potential) as well as temperature. It was found that temperature is a more important parameter than initially thought, and methanol production increases considerably when the temperature is elevated above its boiling point, most likely related to its adsorption strength, and controlling the water balance in the cell is also very important. The team has made several key cell innovations that have improved performance, which in this case is the rate of oxygenate formation – including obtaining new commercial and custom membranes and optimizing catalyst composition. This project has also had a broader impact on our group and effort. In the past year, we expanded our effort and have started collaborating with Chinbay Fan's group at GTI for cell and process scale up. The team has also found that given alternative anode catalysts, our system is an efficient electrochemical concentrator and CO_2 compressor; some work has been put into proof of concept of this device. There

has also been an unexpected synergy with the NiO/ZrO₂ composite materials that are core to this project and some energy storage work going on in our group; in short, we have used the new structures formed in this Early Career project to improve the performance of metal oxide Li-ion batteries.

Water Splitting by Thin Film Metal-Oxo Catalysts

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Funding: \$209,000 (2014)

PROGRAM SCOPE

The scope of this project is to elucidate the mechanism of the oxygen evolution reaction (OER) by catalysts comprising self-assembled, the metal oxidic films (M-OEC catalysts). We have examined catalysts comprising the metals Mn, Ni and Co and have sought to uncover the chemical principles that underlie the electrodeposition of M-OECs and their mechanism of action in neutral or near neutral conditions. The project scope entails experiments aimed at addressing eight questions: (1) what are the mechanistic pathways for oxygen evolution mediated by M-OEC thin films; (2) what are the mechanistic pathways that govern the facile electrosynthesis of M-OECs; (3) how does charge and mass transport occur through electrodeposited films of these catalysts; (4) what are the periodic trends that underpin efficient OER catalysis; (5) can the metal ion composition of the OEC be used to systematically control activity, selectivity, and mechanism for the OER; (6) what is the role of proton-coupled electron transfer (PCET) in enabling efficient OER catalysis at intermediate pH; (7) how does the pH and electrolyte composition impact catalyst stability; and (8) can favorable equilibria be established such that OEC materials heal themselves. All of these questions bear particular relevance to the preparation, efficient operation, and longer-term stability of new water splitting catalysts.

FY 2014 HIGHLIGHTS

We continue to meet the goals of the program with the accomplishments described below for catalysts comprising the metals Mn, Ni and Co. Cobalt catalysts: Differential Electrochemical Mass Spectrometry (DEMS) and in-situ isotopic labeling studies have been performed to shed light on the microscopic oxygen formation step in OER by Co-OEC. The major OER pathway involves coupling of terminal oxygens, which are supplied from water solvent and the minor pathway involves coupling of ¹⁸O atoms present within the Co-OEC catalyst to terminal ¹⁶O from water. Synchrotron-based grazing incidence X-ray diffraction (GID) reveal that the Co-OEC films are composed of uniformly stacked nanoparticles of the catalyst. Motivated by the recent reports of Co cubanes behaving as WOCs we undertook OER studies and showed that the OER activity is not due to the cubane but rather to Co(II) impurities, which form the Co-OEC. A second important conclusion of this study is that when glassy carbon electrodes are used as anodes in OER studies, degradation of the electrode surface to form CO₂ can occur. Manganese catalysts: An active Mn-OEC has been developed for strong acid solutions by defining the nucleation and growth kinetics rate law as compared to the OER rate law. At pH = 0, the OER potential is sufficient to ensure that the catalyst will nucleate and grow (i.e., self-heal) thus delivering the first acid stable OER catalyst using non-critical materials. The mechanism of Mn-OEC electroactivation has been defined. It involves a comproportionation of MnO₂ and Mn(OH)₂ to produce Mn₂O₃ or Mn₃O₄. Nickel catalysts: We

have elaborated the OER mechanism of Ni-OECs by using high-energy X-ray scattering and pair distribution function analysis to identify the structure of the activated catalyst definitively and used this data together with DEMS data to provide insight into the mechanism of the O₂ formation process itself.

Catalytic Applications of H Atom Transfer from Transition-Metal Hydride Complexes

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Funding: \$160,000 (2014)

PROGRAM SCOPE

The goal of the project is to understand how transition-metal hydrides are regenerated from transition-metal compounds and hydrogen. We have shown that, in the presence of trityl radicals (Ar₃C•), a cobaloxime (CoII) reacts with H₂ to generate a species capable of transferring H• to those radicals. We are studying at high H₂ pressures the equilibrium for H₂ addition to cobaloximes, trying to characterize the species responsible for H• transfer. We will look for H/D exchange between hydrogen gas and the O-H-O hydrogen bonds in Co(dmgh)₂. Investigating whether chromium radicals CpCr(CO)₃• can catalyze H₂/D₂ exchange will help us test the mechanism we have proposed for the activation of dihydrogen by chromium radicals. We will also test a related hypothesis, that the sterically encumbered (C₅Ph₅)Cr(CO)₃• cannot cleave H₂. We have shown that the V-H bond is weak enough to be a good H• donor. However, the weakness of that V-H bond makes it difficult for •V(CO)₄(P-P) to cleave H₂. We will attempt to reduce •V(CO)₄(P-P) in the presence of weak acid and thus to regenerate V-H.

FY 2014 HIGHLIGHTS

Axial ligands have effects on the ability of cobaloximes to generate transferable H atoms from H₂. An active cobaloxime catalyst contains one and only one axial ligand. Co(dmgbF₂)₂ will coordinate only one Ph₃P; the addition of additional Ph₃P (beyond 1 equiv) to a solution of Co(dmgbF₂)₂ does not affect its turnover in catalyzing H• transfer from H₂. We have examined the UV-vis spectra of Co(dmgbF₂)₂ in CH₃CN under hydrogen pressures up to 70 atm; a Co(I) compound with an exchangeable proton is eventually formed. We have determined the bond dissociation free energy and pK_a of the cobaloxime-H bond in that new Co(I) compound to be 50.5 kcal/mol and 13.4, respectively, in CH₃CN, in agreement with previous reports.

Templating Routes to Supported Oxide Catalysts by Design

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Funding: \$100,000 (2014)

PROGRAM SCOPE

Supported oxide catalysts constitute a large and important family of catalytic materials, and they are applied to a number of fuel- and energy-relevant areas, such as the production of energy-intensive basic chemicals and feedstocks from biomass or petroleum crudes, emissions controls needed in automotive and power generating stations, and in upgrading fuels or synthesizing fuel additives. This program on 'Templating Routes to Supported Oxide Catalysts by Design' seeks to understand and control the design rules for oxide-oxide interfaces so that more active and selective catalysts may be synthesized and used to solve pressing energy needs. The program encompasses three areas: 1) developing new methods to quantify and then to increase the number of active species in a mixed oxide catalyst sample, 2) developing new methods into hard-to-synthesize catalyst morphologies from pre-built cluster precursors, and 3) developing new classes of catalyst materials via nanocavity oxide supports. These three areas target gaps in our knowledge of atomically-precise syntheses and the resulting synthesis-structure-function relationships, specifically where the catalytic oxides cannot be adequately described as either isolated cations transition or extended crystallites. It is in this range of compositions that catalytic activity is strongly dependent on the catalyst atomic structure, and also where there are the greatest opportunities for developing new or better controlled reactivity. This program seeks to give researchers new methods of atomically-precise synthesis and tools to make quantitative comparisons of catalyst syntheses and thus to rationally develop new materials. These techniques promise better control of these catalysts at the atomic scale, which in turn offers to improve the efficiency of these processes and to lead to new catalysts required for the evolving energy and fuels landscape.

FY 2014 HIGHLIGHTS

Four areas of supported oxide catalysts were advanced in FY 2014. First, building off prior BES-supported work, we demonstrated novel FeO_x-ceria catalysts with improved performance in the reduction of NO, as relevant for emissions treatment, and developed corresponding quantitative structure-reactivity correlations. (Applied Catalysis B). In a related approach, we showed that that highly dispersed TiO_x, TaO_x, or MoO_x on alumina improve Pd-catalyzed denitrogenation (Catalysis Letters), as relevant for the processing of hydrocarbon fuels. In parallel, we then developed two related techniques where phenylphosphonic acid chemisorption quantifies a) the number of solvent-accessible TiO_x in mixed oxides (J. Catalysis) and b) the subset of these that are undercoordinated and therefore participate in oxidation reactions (ChemCatChem). These are the first studies to directly give the active fraction of sites in a mixed oxide Lewis acid catalyst, and we showed that the fraction of TiO_x participating in the reaction could be as low as 20% of those that were physically accessible to reactants. We have begun exploration of a novel cluster precursor to supported CuO_x catalysts, and in preliminary work, it has demonstrated unusual activity in NO reduction and cyclohexane oxidation. Finally, we have leveraged our prior demonstration that 1-2 nm nanocavities in an alumina film on titania impart reactant selectivity to photocatalytic oxidations and reductions. Here we selectively photodeposit Ag nanoparticles on the titania domains in a silica-on-titania material, resulting in smaller, more monodisperse nanoparticles than for controls. The nanostructure of these materials also eliminated significant sintering of the Ag, a key parameter for practical catalyst implementation. (Chemistry of Materials)

Catalytic Growth of Molecular-Scale Wiring

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

The goal of this proposal is to develop catalytic methods for the synthesis of carbon-based nanoelectronic materials. This is a field that is currently limited by the dearth of methods available to cleanly produce atomically defined materials such as carbon nanotubes and graphene ribbons. This proposal tests the hypothesis that ring-opening alkyne metathesis polymerization (ROAMP) can serve as the basis for creating an entire class of new electronic materials. The importance to the Department of Energy and its mission is three-fold. First, the science in this proposal will develop new methodology that will expand the tool kit of catalytic processes and will apply what is learned to problems in Materials Science. Second, this approach will afford tailorable materials useful in nanoscale charge-transport applications such as highly efficient solar cells, single molecule devices, and light emitting diodes. Third, because many of these types of molecules proposed here are unknown (as are the methods to form them), there is potential to discover previously unknown physical phenomena that could have broad impact.

FY 2014 HIGHLIGHTS

This work has been focusing on application in biological labeling.

- i. We have had several important “firsts”. We have developed the first example of a living ROAMP reaction.
 - ii. Further shown that multidentate ligands in the form of salicylimine ligands create more well-behaved living polymerizations.
 - iii. Building from these studies, we recently developed the first new bench stable catalytic system that is able to effect the ROAMP reactions in protic solvents such as methanol and water.
 - iv. We have also begun a detailed mechanistic study of the ROAMP reaction of a dibenzocyclooctadiyne derivative reaction, and have identified a metallotetrahedrane intermediate in the reaction.
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Reactivity & Structural Dynamics of Supported Metal Nanoclusters using Electron Microscopy, In-Situ X-Ray Spectroscopy, Electronic Structure Theories, & Molecular Dynamics Simulations

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Funding: \$640,000 (2014)

PROGRAM SCOPE

In a program of collaborative research, we will develop quantitative understanding of the complex dynamical attributes of the atomic and electronic structures of supported metal-cluster catalysts as they exist under operando conditions. We will focus on supported mono- and bimetallic clusters in sub- to 5nm size range. Our goals are: 1) Unveiling the correlations between dynamic structure, electronic properties, and reactivities in nm-scale catalysts; and 2) Development of new analytical methodologies that will test and validate advanced techniques enabled by the NSLS-II synchrotron at Brookhaven National Laboratory and theory-directed means of computational modeling. We will advance the capabilities of spectroscopic, diffractive, and imaging methods based on electron and X-ray probes as well as the time, length, and energy scales required by theory in order to provide predictive simulations, work enabling a new set of unified capabilities for operando characterization. Our work will provide new methodologies for investigating catalysts at work, overcoming limitations in analytical methods that have historically made the characterization of complex materials structures and chemistries over the entangled lengths scales that are important in mechanisms of catalysis extremely challenging. The key focus of our work will be to develop an integrated multiplatform combination of spectroscopy, imaging and scattering methods for use in studies of catalytic reactions carried out under operando conditions. To support the development of a directly-coupled theoretical framework, we will investigate factors affecting the flow of charge between the metal atoms and adsorbates, and the correlations that exist between these factors. Finally, we will examine mechanisms of selected prototypical catalytic reactions. The main result of the entire project will be the benchmarking of a new, state of the art capability for use in mechanistic studies of complex catalytic systems.

FY 2014 HIGHLIGHTS

We have made significant progress in the multidisciplinary efforts to understand the nature of the atomic scale structure and dynamics of nanoscale catalysts. Foremost in this regard is the progress made in our collaborative efforts to establish a validated toolset for the characterization of the nanoscale materials that are found ubiquitously in heterogeneous catalytic processes.

- 1) A. Frenkel and R. Nuzzo have demonstrated the utility of advanced XAS and XES spectroscopies (HERFD and RIXS) as a means through which the complex microscopic attributes of electronic charge distributions in a catalyst, and the mechanisms through which environmental conditions (e.g. temperature and pressure) modify them, can be understood—and further developing new theoretical frameworks for their analysis (together with J. Rehr).
- 2) J. Rehr, A. Frenkel and R. Nuzzo have highlighted the role of first principle simulations (DFT/MD-based) theory in obtaining the links that exist between multiple components of a catalytic system

(e.g. the precise atomic structure of a catalytic cluster, of a supporting oxide, and the bonding patterns of adsorbates) and the properties that are exhibited under reaction conditions.

- 3) J. Yang and R. Nuzzo developed quantitative methods of electron microscopy (e.g. QSTEM, for shape determination in supported metal catalysts and EELS, for studies of catalyst-support interface) that are complementary in nature to XAS-based measurements and provide important single-cluster-specific constraints to theory.
- 4) A. Frenkel and R. Nuzzo have applied XAS *in operando*, to investigate features relevant to catalytic properties, work that includes investigation of temperature and pressure dependent bonding dynamics of supported metal-cluster catalysts to adsorbates and an investigation of structural complexities and reconstructions of the catalysts evidenced in the hydrogenation of ethylene.

Atomic Level Studies of Advanced Catalysts for Hydrodeoxygenation

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Funding: \$160,000 (2014)

PROGRAM SCOPE

The utilization of biomass for the production of fuels and chemicals is currently an area of great activity because of the recognition that fossil fuels are a finite resource and because of the imminent threat of global warming from the release of carbon dioxide. Biomass pyrolysis has great potential for the production of drop-in replacements for petroleum products, but the pyrolysis oil product has low heating value and stability and high corrosivity, and improvements are needed. This project involves the development of advanced hydrodeoxygenation (HDO) catalysts to reduce the oxygen content of the oil. The catalysts that will be developed are a class of highly active and stable materials, the transition metal phosphides. Initial tests in our laboratory and elsewhere have demonstrated that the catalysts are highly effective in oxygen removal from model bio-oil compounds. The specific compounds to be studied are a series of phosphide catalysts (MoP, WP, Fe₂P, CoP, and Ni₂P), as well as advanced bimetallic compositions. The study of bimetallic compositions is motivated by our recent finding that NiFeP has outstanding catalytic properties. The catalysts will be highly dispersed and will be studied by x-ray absorption spectroscopy (XAS). The novel catalysts will be tested with model compounds and the best compositions will be tried in a pilot scale unit with real feeds at realistic pyrolysis conditions. The substrates to be used will be 2-methyltetrahydropyran (2-MTHP) and guaiacol (GCOL), which are respectively models for cellulose and lignin. The work will include detailed studies of kinetics and spectroscopy to understand the mechanism of the HDO reaction and to relate it to the structure of the catalysts in their working state. The overall objective is to obtain information that can be used to improve the catalyst action by understanding the key factors that govern reactivity.

FY 2014 HIGHLIGHTS

Initial studies indicate that the best catalyst is Ni₂P. The temperature dependency of the catalyst activity for 2-MTHF HDO was determined and it was found that at 350°C Ni₂P/SiO₂ showed 100% conversion and 85% selectivity to n-pentane, with higher oxygen removal activity and less C-C bond cracking activity than commercial noble metal Ru/C and Pd/Al₂O₃ catalysts based on the same amount of active sites.

Contact time measurements were used to provide the reaction networks for both 2-MTHF and guaiacol. For 2-MTHF initial ring opening was found to be the rate-determining step and 2-pentanone and n-pentanal were intermediates. For guaiacol phenol HDO was the rate-determining step. Kinetics indicate 2-MTHF and H₂ are competitively adsorbed on surface. Analysis by a rake mechanism showed that 1-pentoxide derived surface species were the most prevalent, and in situ infrared spectroscopy confirmed the predictions.

New Horizons in C-F Activation by Main Group Electrophiles

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

This project expands a novel approach to activation and functionalization of C-F bonds. The key innovative aspect is the departure from the transition metal paradigm in C-F activation. While the thrust of much of the research in the area of well-defined C-F functionalization is in the direction of using electron-rich transition metal complexes, this project relies on an electron deficient main group catalyst and the process does not involve redox changes. Carbon-fluorine bonds are among the most robust functionalities in chemistry owing to their thermodynamic stability and kinetic inertness. Activation of C-F bonds is thus a fundamental challenge of note. It is also often viewed through the prism of remediation of polyfluoroorganic atmospheric pollutants such as chlorofluorocarbons (CFC), hydrofluorocarbons (HFC), and perfluorocarbons (PFC), all of which are very potent greenhouse gases. They are entirely anthropogenic and their sources (as waste) include some key industries, such aluminum, magnesium, and semiconductor production. Our chemistry utilizes highly reactive main group cations (silylium R₃Si⁺ or alumenium R₂Al⁺), or their closest approximation in solution, that engages the fluorine atom in the critical C-F cleavage step. The overall process is a conversion of a C-F bond into a C-H bond (hydrodefluorination or HDF) or into a C-Alkyl bond (alkylative defluorination, or AlkDF).

FY 2014 HIGHLIGHTS

In FY 2014, we focused on three directions. In one, preparative methods for the syntheses of substituted carborane anions continued to be improved. We prepared new derivatives of the RCB11Cl11 anion with different R groups for improved solubilities. In the second, the synthesis of fluorinated triphenylmethyl cations was pursued. We identified these cations as promising activators of X₃SiH silanes where X is a more electron-withdrawing group than a simple alkyl. Practical isolation of these highly reactive species as pure salts has proven challenging, but preliminary indications point to the viability of at least partially fluorinated triphenylmethyl cations. In the third direction, synthesis of triarylaminium salts with carborane anion partners was pursued. Halogenated triarylaminium cations were identified as promising strong one-electron oxidants that may be of wide general use, and of interest within the specific aims of our project as activators of disilanes by oxidation to silylium cations. We have been able to prepare well-defined triarylaminium-carborane salts with aminiums possessing redox potentials of +1.1V and higher vs ferrocene/ferrocenium. Some of this work was carried out by graduate students supported by either

private industrial funds or by a grant from the (private) Welch Foundation, which shares some of the goals with respect to highly reactive cations with the DOE project.

Heteroatom-Doped Carbon Materials as Oxygen Reduction Electro-Catalysts in Acidic and Alkaline Media

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Funding: \$160,000 (2014)

PROGRAM SCOPE

The project is a systematic investigation of the heteroatom-doped carbon structures as electro-catalysts for oxygen reduction reaction (ORR) in acidic and alkaline media, using fundamental approaches based on catalysis, electro-chemistry and computational modeling. Oxygen reduction reaction remains as the major cause of efficiency loss in low-temperature energy conversion devices such as proton exchange membrane (PEM), anion exchange membrane (AEM) and direct methanol fuel cells (DMFC), and metal-air batteries, even when precious-metal catalysts are used as the cathodic electrodes. Our work focuses on two classes of heteroatom-doped carbon materials: those that are doped with one or more heteroatoms (e.g., N, P) without having a metal center as part of an active site and denoted as CN_x (CP_x) and those where a metal is part of the doped carbon matrix, denoted as (Me-N-C) where Me is a transition metal such as Fe or Co. The main objective of the project is arriving at a molecular level understanding of the nature of active sites, the material synthesis steps that create these active sites, and the structural/surface characteristics that impart electro-catalytic activity to these materials. The ultimate goal would be to elucidate the mechanistic steps involved in the oxygen reduction reaction and link them to molecular features over these catalysts.

FY 2014 HIGHLIGHTS

Two different classes of non-precious metal oxygen reduction reaction (ORR) catalysts for Proton Exchange Membrane (PEM) fuel cells, namely nitrogen-containing carbon nanostructures (CN_x) and iron-nitrogen co-ordinated catalysts supported on carbon (FeNC) were studied and compared for their activity and stability using both half and fuel cell tests. FeNC catalysts were found to be more active than CN_x catalysts, but the latter were more stable. The effect of acid-washing on the two was also markedly different: FeNC catalysts showed a significant decrease in ORR activity after washing due to leaching away of Fe from Fe-based sites. On the other hand, a marked increase in activity was noted for CN_x catalysts due to removal of inactive metallic particles blocking the active sites along with the non-conductive oxide support. In addition, various surface and bulk characterization techniques such as X-ray Photoelectron Spectroscopy (XPS), Temperature Programmed Oxidation (TPO), X-ray Absorption Near Edge Spectroscopy (XANES), Extended X-ray Absorption Fine Structure spectroscopy (EXAFS), Mössbauer spectroscopy, Transmission Electron Microscopy (TEM) and Superconducting Quantum Interference Device (SQUID) magnetometry were employed to gain key insights into the two classes of materials. We also used H_2S poisoning as a probe to investigate the nature of active sites in FeNC catalysts and compare and contrast the results with those for CN_x catalysts published previously by our group. FeNC catalysts showed a remarkable decrease in their activity when treated with H_2S attributed to poisoning

of Fe-based active sites in these catalysts due to iron-sulfur binding as also confirmed with XPS and EXAFS. These results were in sharp contrast with those for CN_x catalysts where an increase in activity was noted after H_2S treatment probably attributed to an increase in pyridinic-N species which were previously shown to correlate with activity in these materials.

Fundamental Studies of Metal Centered Transformations Relevant to Catalysis

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PROGRAM SCOPE

The specific objectives and research goals of the project are to obtain information that is relevant to metal mediated transformations that produce useful chemicals from natural resources. For example, considerable effort is currently being directed by researchers towards (1) the implementation of a "hydrogen economy", in which hydrogen serves as a fuel, and (2) the use of ubiquitous carbon dioxide as a renewable carbon source for the synthesis of useful chemicals. However, the practical realization of both of these objectives presents daunting challenges. For example, a principal problem with respect to the utilization of carbon dioxide as a chemical feedstock is concerned with the fact that it is not only thermodynamically a very stable molecule, but it is also kinetically resistant to many chemical transformations. Likewise, the energy efficient storage of hydrogen with a high volumetric energy density is a critical prerequisite to the implementation of a hydrogen economy. The discovery of new catalytic methods for (1) the rapid generation of hydrogen and (2) the functionalization of carbon dioxide are, therefore, crucial for advancing the use of hydrogen as a fuel and for utilizing carbon dioxide as an effective carbon source for commodity chemicals. In addition to improving catalytic efficiency for the above reactions, it is imperative to develop catalysts that do not utilize precious elements that are in short supply, which thereby provides an additional objective of the project.

FY 2014 HIGHLIGHTS

Specific emphasis has been directed towards the discovery of new transformations employing nonprecious metals that are concerned with the reduction of carbon dioxide via bicarbonate, the generation of hydrogen, the disproportionation of formic acid to methanol, and the use of formic acid in transfer hydrogenation reactions. (1) Dehydrogenation, Disproportionation and Transfer Hydrogenation Reactions of Formic Acid Catalyzed by Molybdenum Hydride Compounds: Much recent interest has focused on the use of formic acid as a hydrogen storage medium because it is a liquid at room temperature and, as such, is easy to handle and transport. It is, therefore, of considerable interest to develop more efficient catalysts for the release of dihydrogen from formic acid, which also incorporate earth abundant metals. Indeed, we have demonstrated that a series of cyclopentadienyl molybdenum hydride compounds are catalysts for this transformation. Interestingly, while dihydrogen and carbon dioxide are the primary products of decomposition of formic acid, methanol and methyl formate are also formed. The selectivity for forming methanol/methyl formate relative to dehydrogenation is dependent on the coligands, with the tricarbonyl compound exhibiting the greatest selectivity. The disproportionation of formic acid is a manifestation of a transfer hydrogenation reaction, which has also

been applied to the reduction of aldehydes and ketones. (2) Reduction of Bicarbonate to Formate in Molecular Zinc Complexes: The conversion of carbon dioxide to formic acid and formates has recently received much attention. In addition to the direct reduction of carbon dioxide, the reduction of bicarbonate to formate has also garnered interest due to the fact that bicarbonates are easier to handle than gaseous carbon dioxide. It is, therefore, significant that we have discovered that a zinc bicarbonate complex can be converted to a formate derivative by reaction with phenylsilane.

Controlling Structural Electronic and Energy Flow Dynamics of Catalytic Processes through Tailored Nanostructures

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PROGRAM SCOPE

The research project “Controlling Structural, Electronic, and Energy Flow Dynamics of Catalytic Processes through Tailored Nanostructures” started in a DOE initiative calling for research projects that provide an unconventional approach to the investigation of catalytic processes. Throughout this project we focus on the notion that controlling the dynamics of a catalytic system in a pre-determined fashion may hold the key to fundamental improvements in the efficiency of catalytic reactions. In this context, we consider both the dynamics of reactants, as they undergo chemical transformation at the active sites of a heterogeneous catalyst and our project also strives to highlight the importance of the dynamics of the catalyst, i.e. its constant structural (e.g., morphology, density and nature of surface defect sites) and chemical (e.g., oxidation state of surface atoms, variation in the composition of the surface layer) reorganization during the course of catalyzing a chemical process in a reactive environment. In addition, we believe that control of the flow of energy, typically in the form of electronic excitations, will emerge as an important concept, in particular with regards to photo-activation of catalytic reactions, as set forth in the DOE Catalysis for Energy report. In this context we develop methods for the catalytic growth of MoS₂ monolayers as photon-harvesting components.

FY 2014 HIGHLIGHTS

The main thrust of our joint experimental and theoretical research effort has focused on the chemical/catalytic activity of MoS₂ and its modifications through defects, reconstruction/sulfur loss and adsorbates. We have identified a Mo₂S₃ surface structure that, though meta-stable, can persist in the presence of adsorbates - such as formic acid, anthraquinone, etc. - even at temperatures at which they constantly bind and desorb. This molybdenum-sulfur compound (MoSC) exhibits far higher affinity to adsorbates even than the step edges of MoS₂, suggesting that if MoSC of this or similar composition can form under catalytic conditions, they may actually carry the bulk of the material’s activity. Following this finding, and other work on MoSCs, the question of the origin of the activity of MoSC has gained renewed momentum and scrutiny. We have highlighted the effect of vacancy clusters and alkali dopants (experimentally and theoretically) in controlling the electronic structure of MoS₂. Our theoretical work predicts defect-laden MoS₂ to be chemically reactive. Furthermore, the joint-edges formed between two sheets of MoS₂, also show interesting metallic and magnetic properties. We have also completed a

project on understanding the nature of the reactive sites for methanol decomposition on titania supported Au nanoparticles. In the same vein, to understand further the factors that control chemical reactivity and selectivity for ammonia decomposition on RuO₂(110) under ambient conditions, we have applied our *ab initio* approach for modeling of reaction rates. In the past year, our experimental investigations have applied three sets of strategies: atomic scale imaging, temperature dependent photoluminescence and x-ray absorption spectroscopy, and photoluminescence imaging. These have been complemented by theoretical modeling and simulation of the same systems using *ab initio* electronic structure calculations based on density functional theory (DFT).

EARLY CAREER: Computational Design of Graphene-Nanoparticle Catalysts

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PROGRAM SCOPE

The overall goal of this project is to develop a systematic computational approach for the rational design of nanoscale transition-metal catalysts supported on graphene, a two-dimensional sheet of carbon atoms arranged in a honeycomb lattice. The use of graphene, as compared to traditional carbon supports, has been experimentally shown to enhance significantly the catalytic activity of metal nanoclusters in fuel cell electrodes. However, there is no clear mechanistic understanding of the role played by graphene supports in improving catalyst performance. This project will develop and implement computational models to understand and predict electronic interactions between transition-metal nanoclusters and graphene supports, taking into account practical complexities that arise from statistical variations in cluster size and morphology, quantum size effects at the nanoscale, and the presence of physical and chemical defects in graphene. Model transition metal/graphene catalysts will be employed for statistical sampling of selected reactions pathways to probe the influence of substrate-cluster interactions on reaction thermodynamics and kinetics. The fundamental understanding gained from these studies could guide the rational design of superior, graphene-supported, transition-metal nanocatalysts with potential applications in energy conversion pathways for alternative fuels.

FY 2014 HIGHLIGHTS

We have made substantial progress in three areas: 1) understanding CO oxidation graphene-supported Pt clusters, 2) establishing thermodynamic pathways for methanol decomposition on Pt clusters, and 3) development of genetic algorithms for global structural optimization of graphene-supported Pt clusters. We performed DFT studies of CO binding on unsupported and graphene-supported Pt clusters using extensive statistical sampling to account for variability in coordination of surface Pt atoms. Defective graphene supports were shown to substantially reduce CO binding energies due to a downshift of the cluster d-band center, which is a direct consequence of strong Pt-C bonds at the defect. We studied CO oxidation on supported and unsupported Pt clusters and found a preferred mechanism without the involvement of adsorbed oxygen precursors. The barriers for this mechanism were found to be lower on defective graphene-supported Pt clusters in agreement with thermodynamic calculations. The results were reported in one journal publication, a PhD thesis, and three conference presentations, with a

second publication in review. DFT studies are now underway to establish the thermodynamic pathways and reaction mechanisms of the full gas-phase methanol decomposition reaction on graphene-supported Pt clusters and establish a direct link with experiments. Separately, we implemented a Genetic Algorithm (GA) to calculate low-energy isomers of supported clusters. As ultra-small Pt clusters do not adopt high-symmetry structures as commonly assumed, a more robust approach for calculating ground-state structures is desirable. Our GA combines inexpensive empirical potentials for initial screening followed by more careful DFT optimization. A noteworthy feature of our GA is that it interfaces directly with the widely used, open-source LAMMPS software. As LAMMPS supports a wide range of interatomic potentials, our approach greatly simplifies portability of the GA to different materials.

Exploiting the Flexibility and the Polarization of Ferroelectric Perovskite Surfaces to Achieve Efficient Photochemistry & Enantiospecificity

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PROGRAM SCOPE

This project applies state of the art quantum mechanical modeling to the study of heterogeneous chemical transformation processes on complex surfaces. Three attributes make this a unique and transformative approach to small molecule heterogeneous photocatalysis for energy and new surfaces for enantiomer separation: 1. The proposed catalysts are new complex oxide alloys whose optical properties have been optimized to enable visible light absorption and excited electron or hole transport to the surface for redox photochemistry. 2. These materials have bulk electric polarization, and the resulting surface charge triggers surface reconstructions that are highly favorable to redox catalysis. 3. The polarization can be reoriented relative to the surface, enabling reversible rumplings, stoichiometry changes, and handedness at the surface. Integrating these positive features, two main projects are proposed: exploring the surfaces of multi-component complex oxides $(A,A')(B,B')O_3$ for photocatalytic splitting of CO_2 and H_2O , and pioneering new surfaces for the separation of racemic mixtures into enantiomers. These projects have the potential to provide efficient chemical fuels from solar energy, and to reduce the costs of medicines and other chiral chemicals.

FY 2014 HIGHLIGHTS

The development of increasingly sophisticated techniques to synthesize and analyze oxide surfaces gives us the ability to engineer surfaces for heterogeneous catalysis. Another critical requirement in this endeavor is a deep thermodynamic and kinetic understanding of surface reconstruction behavior. We explore the reconstruction behaviors of Ti-based perovskite type oxides: $BaTiO_3$, and $PbTiO_3$, which exhibit ferroelectricity. We investigate the effect of their switchable polarization, in addition to the effects of temperature and the chemical potentials of their constituent elements. We find that these oxides undergo surface reconstruction transformations that generally result in enrichment of their catalytically active component (Ti). An applied electric field changes the material's polarization, which then alters the surface electronic properties, and thereby affects their sensitivity towards stoichiometric

changes. We also demonstrate kinetic tunability from a particular surface phase coexistence observed in BaTiO₃, namely the *c*(2×2) and *c*(4×4), where the diffusion behavior of the TiO units that compose both surfaces strongly dictate their degree of agglomeration. Ultimately, we wish to use these well-defined surface reconstructions in heterogeneous catalysis, for example in electrolytic water splitting, or generation of H₂ and O₂ from water using electrical work, which requires two different catalysts. One catalyst enhances oxidation (O₂ evolution reaction), the other enhances reduction (H₂ evolution reaction), and both are expected to perform optimally and stably in the same chemical condition. We studied the interaction of water with a reduced, TiO₂-terminated surface reconstruction of BaTiO₃ containing Ti adatoms using density functional theory. In this study, we found that water could oxidize the undercoordinated surface Ti adatoms through four possible channels: molecular adsorption, dissociative adsorption, acid-base reaction, and oxidative adsorption.

Supramolecular Ensembles in Catalysis

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Funding: \$180,000 (2014)

PROGRAM SCOPE

The project “Organometallic and Catalytic Chemistry of Functionalized Complexes” consists on three subprojects focused on applications of specialty ligands. The program advances the theme that transformations of small molecules are most efficiently catalyzed by complexes of ligands that control redox, proton-transfer, and π -donation. The first project addresses fundamental questions associated with how electron-transfer influences reactions of homogeneous catalysts. We introduce a new redox-active ligands of the type FcCH₂PR₂ where Fc is a modified ferrocene. These ligands are less non-innocent and more easily installed than traditional non-innocent ligands. The second project, which grew from work in the previous contract period, explores the formation and reactivity of a diphosphine-dialkoxide platform derived from coupling of phosphine aldehydes. This study promises to deliver a sterically and electronically novel platform. The third project focuses on an acyl-pyridinol ligand for controlling reactivity of iron hydride. The effort exploits a new route to a close mimic of a cofactor in a biological hydride transfer catalyst and examines associated tautomeric equilibria.

FY 2014 HIGHLIGHTS

We synthesized a new family of RuNi dithiolates featuring geometrically flexible Ni centers that enable both acid-base and redox chemistry, behavior which is characteristic of the hydrogenases. Crystallographic characterization of these compounds revealed short Ru–Ni distance and tetrahedral Ni sites. Variable temperature NMR studies show that the Ni center is rigid. The reduced complexes are highly basic. The mixed valence Ru(II)Ni(I) complex, a structural model for the Ni-L state of the [NiFe]-hydrogenases, was characterized crystallographically, spectroscopically, and in terms of its reactivity. Measurements indicate that these cations are described as Ru(II)–Ni(I). Correspondingly, the neutral precursor is best described as Ru(II)Ni(0). The fast electron self-exchange rate of 107 M⁻¹s⁻¹ between [1]⁰ and [1]⁺ confirms the minor reorganization associated with this redox, consistent with a Ni(0)/Ni(I) oxidation.

Fundamental Studies of Oxidation Reactions on Model Catalysts

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

The discovery by Haruta more than a decade ago that by co-feeding H₂ with propylene and O₂ and using Au/TiO₂ as the catalyst, one can produce PO with high selectivity provides the potential for a single-step, direct and green solution to this long standing catalytic partial oxidation challenge. Moreover, the catalytic chemistry of this system offers unique opportunities to study the role of *in situ* generated hydrogen peroxide as a selective olefin oxidant and to probe the catalytic properties of nanometer and subnanometer metal particles. We focus here on Au/TS-1 catalysts, which display the improved stability and activity associated with isolated Ti centers, and probed the nature and location of the active Au. Since proximity of Au and Ti is required for the catalysis, the activity of Au on a support made by coating TS-1 with an S-1 shell showed that Au clusters small enough to enter the MFI pore structure are active for PO production. Addition of Au to uncalcined TS-1, the pores of which were still blocked by the template, led to an unprecedented 20 hour activation period. Correlated changes in apparent surface area and other supported data showed that peroxide generated from H₂ and O₂ over the Au particles burned some of the template out of the pores, allowing Au migration to the Ti anchor points that create the active sites in the pores. Analysis of the most active catalysts yet reported, with a rate of reaction of 300 g_{PO} h⁻¹ kg_{cat}⁻¹, showed that the Cs salt used in deposition precipitation of the Au in these catalysts helps to stabilize the small Au particles in the TS-1 pores, thus maximizing the number of stable Au sites. These studies all confirm the importance of Au clusters small enough to enter the TS-1 pore structure as active sites for propylene epoxidation.

FY 2014 HIGHLIGHTS

Recent work has focused on three areas. The first is closure of the work on Au supported on uncalcined TS-1 supports, Au/U-TS-1. The motivation for that work was to force the gold to be deposited on the outer surface of the TS-1 crystallites by blocking the interior pore structure by not removing the template around which the TS-1 structure grows during its synthesis. Second is elaboration of the discovery that the reaction rate of Au/TS-1 can be dramatically enhanced by using Cs₂CO₃ instead of our standard Na₂CO₃ as the pH control agent during the deposition precipitation (DP) of the Au. The third is examination of the effects of the residual Na left from the standard DP process, the Cl left from the chloroauric acid gold precursor, and the method of activation.

Influence of Multi-Valency, Electrostatics and Molecular Recognition on the Adsorption of Transition Metal Complexes on Metal Oxides: A Molecular Approach

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Funding: \$150,000 (2014)

PROGRAM SCOPE

The synthesis of heterogeneous catalysts is comprised of numerous unit operations, all of which impact the properties (morphology, metal particle size, distribution) of the final catalyst and ultimately its catalytic performance. The absence of knowledge of the molecular details that transforms a transition metal complex (TMC) and support material (metal oxide or carbon) into a functioning catalyst hinders our ability to synthesize catalysts with desired properties (i.e., average particle size and monodispersity). The initial association (or adsorption) of transition metal precursors onto the support surface during catalyst synthesis has received very little attention. We have examined the molecular level details of catalyst synthesis with a significant emphasis on the chemistry that occurs at the solid-liquid interface during the initial adsorption of transition metal complexes. The mechanism (outer-sphere, electrostatic, inner-sphere) by which TMCs adsorb to neutral and charged solid-liquid interfaces will be examined. The objectives of the proposal are (1) to quantify TMC adsorption on charged metal oxide interfaces under electrostatic conditions utilizing isothermal titration calorimetry (ITC); (2) measure and quantify TMC speciation in solution via capillary electrophoresis; (3) assess the kinetics of TMC adsorption at charged interfaces via in-situ streaming potential measurements; (4) quantify molecular recognition and multivalency during inner-sphere adsorption of siloxide-based and organometallic TMCs with ITC; (5) quantify the influence of adsorption mechanism on particle growth and final particle size during pretreatment (drying, calcination, reduction) by synchrotron-based x-ray absorption and scattering. The in-situ approach will provide a direct correlation between the mechanism of TMC adsorption and the pretreatment regime with the overall properties of the final catalyst.

FY 2014 HIGHLIGHTS

We have continued to develop the isothermal titration calorimetry technique to measure the adsorption of solvated transition metal precursors to amphoteric oxides. In collaboration with Tom Mallouk (PSU chemistry), we demonstrated that the final particle size and the dynamics of particle sintering of Rh was correlated to the measured heat of adsorption on Dion-Jacobsen perovskites. Interestingly, the difference in the heat of adsorption is quite small but lead to drastically different final particle sizes after reduction. We have continued this work on perovskites by sampling across the periodic table examining both early and late transition metal precursors. The interactions between Rh and the other transition metals is covalent in nature as previously suggested by XPS and confirmed by x-ray absorption spectroscopy. In a parallel study, we have used ITC and adsorption isotherms of cationic and anionic Pt precursors on silica and alumina as a function of pH; adsorption under this situation is dominated by electrostatic forces. Once again, we have confirmed that the solution conditions during adsorption influences the overall thermal behavior of the catalyst. With the appropriate choice of transition metal precursor, the greater the difference between the solution pH and PZC of the support, the greater quantity of adsorption and the higher the precursor heat of adsorption (normalized per mole). At a maximum pH/PZC difference, there are minimal changes in the quantity of precursor adsorbed, but significant differences in the measured heat of adsorption. This is manifested in significant differences in particle size at comparable surface coverage. The thermodynamics of the precursor adsorption under electrostatic conditions appear to be independent of metal identity, but highly dependent on the inner-sphere ligands. We continue to pursue a quantitative understanding of electrostatic adsorption in order to refine proposed mechanisms.

Lewis Acid Pairs for the Activation of Biomass-derived Oxygenates in Aqueous Media

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PROGRAM SCOPE

The objective of this project is to understand the mechanistic aspects behind the cooperative activation of oxygenates by catalytic pairs in aqueous media. Specifically, we investigate how the reactivity of a solid Lewis acid can be modulated by pairing the active site with other catalytic sites at the molecular level, with the ultimate goal of enhancing activation of targeted functional groups. A main goal of this work is to devise rational pathways for the synthesis of porous heterogeneous catalysts featuring isolated Lewis pairs that are active in the transformation of biomass-derived oxygenates in the presence of bulk water. Achieving this technical goal requires closely linking advanced synthesis techniques; detailed kinetic and mechanistic investigations with comprehensive characterization studies of both materials and reaction intermediates. Two technical aims are pursued: 1) Coupling Lewis and Brønsted acid sites for enhanced transfer hydrogenation chemistry. Tin- or zirconium-containing zeolites (e.g., Sn- and Zr-Beta) are active transfer hydrogenation catalysts. We demonstrate an integrated catalytic process for the efficient production of gamma-valerolactone (GVL) from Furfural (Fur) via sequential transfer hydrogenation (TH) and hydrolysis reactions triggered by zeolites with Brønsted and Lewis acid sites. 2) Pairing Tin/Borate Lewis acid pairs for the selective epimerization of carbohydrates. When paired with homogeneous Lewis acidic borates, Sn-Beta promotes 1,2 intramolecular carbon shifts in carbohydrates wherein a bond between C-1 and C-3 is formed, with C-1 moving to the C-2 position with an inverted configuration. We perform mechanistic studies interrogating the structure of Sn-O-B-O-Si active site and its interaction with hexoses and pentoses. In addition, the use of dynamic nuclear polarization nuclear magnetic resonance is introduced for the analysis of Sn-containing zeolites prepared with natural abundance ^{119}Sn precursors.

FY 2014 HIGHLIGHTS

- Demonstrated the first example of dynamic nuclear polarization NMR for the characterization of zeolites. Published in JACS 2014
- Performed a detailed kinetic evaluation of the transfer hydrogenation chemistry with solid Lewis acids to produce gamma-valerolactone

Towards Realistic Models of Heterogeneous Catalysis: Simulations of Oxidation Catalysis from First Principles

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Funding: \$160,000 (2014)

PROGRAM SCOPE

The primary goal of this program is to develop more robust, validated models of energy-related catalytic reactions at metal surfaces. We focus on the catalytic chemistry of molecular oxygen (O_2), because catalytic oxidations are a central element of environmental catalysis (e.g. of functionalizing feedstocks, of operating fuel cells, or of cleaning the exhaust from an internal combustion engine), and because reliable, quantitative models have been elusive. Noble metals (Pt, Pd, Ag, ...) are the most common metals used for catalytic oxidations, but the detailed mechanisms by which these function, how reaction mechanisms depend on the structure and composition of the catalyst, and how temperature, pressure, or other reaction conditions effect these mechanisms, are not well understood either qualitatively or quantitatively. The objective of this work is to produce a conceptual framework and mathematical models that reliably describe and predict the environment-dependent mechanisms and rates of catalytic reactions of oxygen over a range of catalytic materials. Achieving this objective will facilitate the design and discovery of superior performing, more robust, and less expensive catalysts, as well as provide the insights necessary to more efficiently design and interpret experiments. We use the catalytic oxidation of NO to NO_2 as a relatively simple yet practically important model, but the implications extend outside this particular context. While the focus here is on oxidation catalysis, the methodologies are applicable to any heterogeneous catalysis.

FY 2014 HIGHLIGHTS

Progress in FY 2014 occurred along three primary fronts.

- 1) We reported new applications of our 'coverage-aware' kinetic models. We used our previously published results for oxygen adsorption on Pt to demonstrate a method to reliably predict temperature-programmed desorption spectra. We further extended the oxygen adsorption DFT models to all the late transition metals and used the results to predict the relative rates of NO oxidation over those metals.
- 2) Energies extracted from DFT do not account for the finite temperature effects that contribute to adsorption free energies, and several recent publications suggest that conventional free energy approximations are substantially in error at temperatures relevant to catalysis. To address these problems, we used DFT and statistical mechanics to compute these free energies exactly. Further, we developed an approximate approach that is no more expensive than the methods used today and that provides much more reliable results.
- 3) The models described above are limited to the description of adsorbate chemisorption. Yet it is known that under some circumstances adsorbates can reconstruct surfaces. Predicting the conditions under which such rearrangements happen, and their quantitative impacts on observed catalytic reactivity, remains a significant challenge. We used a cluster expansion approach to discover the evolution of surface structure with O coverage on Pt(111), encompassing both chemisorbed and Pt "reconstructed" adsorbates. The model correctly recovers the chemisorbed structures found before, recovers the O-induced reconstructions previously identified, and discovers new, stable reconstructed forms. This model can now be used as a basis for understanding the kinetics of the surface reconstruction and its decomposition.

The Polymerization of Olefins and Alkynes with New Alkylidene Catalysts

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PROGRAM SCOPE

A major application of well-defined (isolable with designed activities) metathesis catalysts is ring-opening metathesis polymerization (ROMP). We have developed a large number of metathesis catalysts with the object of controlling the stereoregularity of polymers prepared through ROMP. The object has been to prepare homopolymers that have essentially a single structure. Currently all cis polymers can be prepared with two possible tacticities. We plan to expand the design of catalysts in order to allow us to prepare all four major polymeric ROMP structures derived from a wide variety of norbornadienes or norbornenes. The next level of control is to prepare polymers from two different monomers to give AB copolymers, again with a single structure. Since polymer properties are dictated by polymer structure, we predict that precise control of polymer structure will have major implications in the design of specialty polymers for a wide variety of applications that have emerged in the last decade in which atactic ROMP polymers have been employed.

FY 2014 HIGHLIGHTS

Among the major accomplishments in the last year is the ability to synthesize polymers through ROMP with pure cis, syndiotactic or cis, isotactic structures. Most recently we have been able to prepare polymers with these structures from dicyclopentadiene, norbornene, and tetracyclododecene; all are monomers that yield tactic polymers, the hydrogenated form of which can be crystalline and high melting. A third structure that has now been achieved is an AB polymer with a cis, syndiotactic structure in which A and B are enantiomers. This has become possible with catalysts that are chiral at the metal and whose chirality inverts with each insertion step. The chirality at the metal controls, through a diastereomeric relationship, which enantiomer is inserted in the each step. Finally, for the first time we have been able to prepare perfectly alternating stereoregular AB copolymers in which A and B are two different monomers. This is possible because of the fact that Mo and W catalysts exist in two isomeric forms that are in equilibrium with one another through rotation about the M=C bond. Monomer A reacts with one form (anti) selectively to give a trans C=C bond and the other form (syn), which then reacts selectively with monomer B to give the second trans C=C bond and the other form (anti) back again. We hope to be able to extend this approach to the synthesis of perfectly alternating conjugated copolymers in which (for example) A is an electron donor and B is an electron acceptor.

High Temperature Chemistry of Aromatic Hydrocarbons

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Funding: \$50,000 (2014)

PROGRAM SCOPE

The primary goal of this research is to uncover all the principal reaction channels available to polycyclic aromatic hydrocarbons (PAHs) at high temperatures in the gas phase and to establish the factors that determine which channels will be followed in varying circumstances. The efficient production of clean energy from fossil fuels will remain a major component of the DOE mission until alternative sources of energy eventually displace coal and petroleum. Hydrocarbons constitute the most basic class of compounds in all of organic chemistry, and as the dominant species in fossil fuels, they figure prominently into the programs of the DOE. Much is already known about the normal chemistry of hydrocarbons under ambient conditions, but far less is known about their intrinsic chemistry at temperatures close to those reached during combustion. An understanding of the fundamental molecular transformations, rearrangements, and interconversions of PAHs at high temperatures in the gas phase, as revealed by careful studies on small, well-designed, molecular systems, provides insights into the underlying chemistry of many important processes that are more complex, such as the generation of energy by the combustion of fossil fuels, the uncatalyzed gasification and liquefaction of coal, the production of fullerenes in fuel-rich flames, and the formation of soot and carcinogenic pollutants in smoke (e.g., benzo[a]pyrene). The rational control of any of these processes, whether it be the optimization of a desirable process, such as the recent commercialized combustion synthesis of C₆₀ and other fullerenes, or the minimization of an undesirable one, requires a clear knowledge of the basic chemistry that governs the fate of the species involved. Advances in chemistry at the most fundamental level come about primarily from the discovery of new reactions and from new insights into how reactions occur. Harnessing that knowledge is the key to new technologies and carbon-rich materials.

FY 2014 HIGHLIGHTS

Our latest research has focused on elucidation of the mechanism of acene-to-phenacene rearrangements of aryl radicals, a fundamental class of skeletal reorganization of polycyclic aromatic hydrocarbons (PAHs) that was recently discovered in our laboratory. To test our hypothesis for the mechanism of this new class of rearrangements, we synthesized 9-bromo-9-[¹³C]anthracene, 1-bromo-1-[¹³C]naphthalene, and 7-bromo-7-[¹³C]benz[a]anthracene and studied their chemical behavior at high temperatures in the gas phase under conditions of flash vacuum pyrolysis (FVP). All three syntheses involved the capture of ¹³CO₂ by a Grignard reagent as the key step for incorporation of the ¹³C isotopic label. Several steps were required to synthesize each Grignard reagent, and several additional steps were then required to convert the intermediate ¹³C-labeled carboxylic acids to the FVP precursors. FVP of 9-bromo-9-[¹³C]anthracene produces two and only two isotopomers of ¹³C-labeled phenanthrene: 4a-[¹³C]phenanthrene and 9-[¹³C]phenanthrene, and that is precisely the result predicted by our mechanistic hypothesis. The major product is 4a-[¹³C]phenanthrene, and the only other significant product is 9-[¹³C]phenanthrene. These two isotopomers are formed in a 60:40 ratio. The lesser amount of 9-[¹³C]phenanthrene reflects the slow but competitive intervention of a 1,3(peri)-hydrogen shift at the stage of the 9-anthracenyl radical. Earlier studies in our laboratory predicted and demonstrated experimentally the 1,3(peri)-hydrogen shift rearrangement in other aromatic hydrocarbons, so we were expecting it to show up here, too. The results of our FVP experiments with 1-bromo-1-[¹³C]naphthalene, and 7-bromo-7-[¹³C]benz[a]anthracene were likewise entirely consistent with predictions based on our proposed mechanism. We conclude from these experiments that acene-to-phenacene rearrangements of aryl radicals do involve the rupture of ring-fusion bonds in cata-condensed PAHs at high temperatures.

Hierarchical Design of Supported Organometallic Catalysis for Hydrocarbon Transformations

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Funding: \$550,000 (2014)

PROGRAM SCOPE

This project aims to decipher the structure and behavior of active sites in supported metal oxide catalysts by synthesizing and studying well-defined and uniform sites. This effort, in turn, will create the insight necessary to prepare heterogeneous catalysts that are more uniform and therefore more active and selective, while remaining both self-activating and regenerable. Our goal requires a close integration of organometallic synthesis and surface chemistry, the best available structural characterization techniques and detailed reactivity studies (kinetics, mechanisms). An essential element of this work is the exploration, using computational approaches, of the plausibility of our structural and mechanistic proposals, both for the correct interpretation of experimental results and to suggest new research directions. The latter is particularly important in terms of understanding the origin of self-activation in the active sites.

Specific objectives include (1) understanding the origin of self-activation in heterogeneous single-atom catalysts for olefin metathesis and polymerization, such as $\text{Re}/\text{Al}_2\text{O}_3$ and Cr/SiO_2 , and (2) designing computational models for these amorphous materials that inform and predict catalyst response to changes in preparation protocols and/or reaction conditions. We also aim to (3) develop new spectroscopic and kinetic methods to challenge these materials mechanistically, again with the goal of developing detailed molecular-level understanding of their activation and deactivation processes. Finally, we aim to (4) transfer this understanding to the synthesis of new catalytic materials based on knowledge of the active site requirements for a given process.

FY 2014 HIGHLIGHTS

We discovered a new, highly active system for olefin metathesis, using chlorinated alumina to support and activate the single-component catalyst CH_3ReO_3 (MTO). We observed a dramatic increase in reactivity for propylene homo-metathesis in a batch reactor, for MTO is grafted on $\text{Cl}/\text{Al}_2\text{O}_3$ compared to $\gamma\text{-Al}_2\text{O}_3$. Furthermore, the increased stability of the metathesis catalyst was easily demonstrated under flow conditions. The cumulative TON for the chlorinated catalyst reached 20,000 after 2,000 min on stream, while it leveled off under 5,000 for the unchlorinated catalyst. Cl seems to prevent deactivation of the Re active sites as well as promote their activity. We also explored the activation of the Phillips ethylene polymerization catalyst Cr/SiO_2 , in which Cr(VI) is reduced to Cr(II) by CO. Using in-situ UV-vis spectroscopy, we showed that reduction proceeds first through a Cr(IV) species at 250°C, then to a Cr(II) species at 320°C. We observed the Cr(II) sites directly for the first time using High Field High Frequency EPR spectroscopy. Upon addition of ethylene, the Cr(II) sites are oxidized quantitatively to Cr(III). The initiating site is a vinylCr(III) species, formed concomitantly with ethyl radicals which, in turn, couple to form n-butane as a byproduct. We also investigated a surface organometallic model for the active sites by grafting $\text{Cr}[(\text{CH}(\text{SiMe}_3)_2)_3]$ onto silica. The supported organochromium catalyst spontaneously initiates polymerization of gas phase ethylene at low pressure (ca. 125 Torr) with a rate law that is first-order in

both $P(C_2H_4)$ and moles of Cr. The specific activity and apparent activation energy of the model catalyst closely resemble that of the conventional Phillips catalyst, suggesting that they share a common polymerization mechanism. Analysis of the products of low-pressure ethylene oligomerization Field Desorption-MS revealed not only integer but also half-integer numbers of ethylene subunits.

Understanding Surfaces and Interfaces of Photocatalytic Oxide Materials with First Principles Theory and Simulations

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Funding: \$180,000 (2014)

PROGRAM SCOPE

The overall goal of this project is to obtain a complete picture of the atomic structure, electronic properties and (photo-)reactivity of transition metal oxide surfaces and oxide-water interfaces. Major specific objectives are: (i) to determine the structure and reactivity of defect-free and defected TiO_2 surfaces and interfaces; (ii) to understand the behavior of photoexcited electrons and holes at TiO_2 surfaces and TiO_2 -water interfaces; (iii) to extend the knowledge gained for TiO_2 to other promising (photo-)catalytic metal oxides.

FY 2014 HIGHLIGHTS

Chemical Dynamics of the First Proton Coupled Electron Transfer (PCET) of Water Oxidation on TiO_2 Anatase - Despite its widespread use in photo-electrochemical water splitting, TiO_2 is not very efficient due to its large overpotential for the oxygen evolution reaction (OER). To understand the origin of this limitation, we analyzed the kinetics of the first PCET, which is the rate-determining step of the OER on TiO_2 . We used a periodic model of the TiO_2 /water interface that includes a slab of anatase TiO_2 and explicit water molecules, sampled the solvent configurations by First Principles Molecular Dynamics, and determined the ET energy profiles by hybrid functional calculations. Our results indicate that the proton and electron transfer are not concerted but sequential. The PT has a significant activation energy, whereas the following ET is essentially barrierless and occurs via an inner sphere process involving a shared hole state. These results also explain the higher OER activity that is observed at high pH.

TiO_2 /Ferroelectric Heterostructures as Catalysts for Water Oxidation – We studied the OER activity of epitaxial heterostructures of TiO_2 anatase on strained polar $SrTiO_3$. Results show that the TiO_2 reactivity is tuned by electric dipoles dynamically induced by the adsorbates during the reaction. The combined effects of these dipoles and epitaxial strain significantly reduce the thermodynamic barriers and improve the OER efficiency.

Mechanism and Activity of Water Oxidation on Pure and Fe-doped NiO_x - Mixed Ni-Fe oxides are promising electrocatalysts for water oxidation due to their low cost and high activity. We studied the OER energetics on selected surfaces of pure and mixed Ni-Fe oxides that are possible candidates for the catalyst's active phase. Based on the computed overpotential, Fe-doped β - $NiOOH$ is even more active than RuO_2 , a well-established OER catalyst, and could thus contribute to the active phase of Fe-doped NiO_x .

Transition Metal Mediated Transformations of Small Molecules

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Funding: \$160,000 (2014)

PROGRAM SCOPE

Catalysis at metal centers is of great scientific, as well as practical, importance because of the high efficiency, high specificity, and low energy demands often associated with such systems. The two major themes of our research are (a) the design of metal-based systems for the synthesis of novel classes of polymers and (b) the identification of new metal-catalyzed systems for the conversion of biomass to fuels and chemicals, and related “green” chemical processes. Recent work encompasses several aspects of organotransition metal chemistry and catalysis. These include (a) the study of steric and electronic effects in ethene/norbornene copolymerization by neutral salicylaldiminato-ligated palladium(II) catalysts and (b) rhodium-catalyzed reduction of sulfoxides to sulfides with HI and CO/H₂. In addition, we have designed new materials to reversibly sense and capture carbon dioxide. We are also addressing key questions concerning the mechanistic steps involved in these transformations.

FY 2014 HIGHLIGHTS

We have discovered a novel one-step process for the reductive deoxygenation of a wide range of organic compounds, including biomass-derived molecules, by a combination of metal catalyst and hydrogen iodide (HI). The mechanism involves close synergy between HI and metal catalyst. HI serves a two-fold purpose: HI acts as a dehydration agent in the initial step of the reaction, and as a reducing agent for the conjugated carbinol group in a subsequent step. Iodine is formed in the reduction step and metal-catalyzed hydrogenation reforms HI. The metal catalyst, in addition to catalyzing the reaction of iodine with hydrogen, also functions as a hydrogenation catalyst for C=O and C=C bonds. We have also discovered a new class of absorbents for carbon dioxide, amino alcohols. They reversibly absorb carbon dioxide at ambient temperature. Carbon dioxide is released back by simply purging the material with air or nitrogen. By coupling the process with a standard pH indicator, the system acts as a sensitive and reversible carbon dioxide sensor with a visual color output. Solid state sensors can be readily fabricated by supporting the amino alcohol and the pH indicator on alumina. This colorimetric response is completely reversible and is not interfered by moisture, oxygen or trace CO₂, present in ambient air.

Late Transition Metal M-Or Chemistry and D6 Metal Complex Photoeliminations

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Students: 0 Postdoctoral Fellow(s), 3 Graduate(s), 0 Undergraduate(s)
Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

This program is focused on the photochemistry of transition metal halo, hydroxo, and hydroperoxo complexes related to solar energy conversion and storage. In particular, reductive elimination reactions of halogens, HOX (X = a halogen), hydrogen peroxide, and water are sought as components of photo-driven, catalytic, endergonic splitting of small molecules.

FY 2014 HIGHLIGHTS

Highlights include:

1. Discovery of a series of platinum(IV) complexes that undergo net photolytic reductive elimination of halogens with record quantum yields.
2. Completion of a mechanistic investigation into the net photo reductive elimination of chlorine that indicated chlorine transfer to alkene traps from a platinum complex excited state.
3. Discovery of the first photo reductive elimination of H₂O₂ (dihydrogen trioxide) from a metal hydroxo-hydroperoxo complex. In addition to being only the second synthetic method for H₂O₂, the O-O bond formation is important component of water to hydrogen and oxygen schemes.
4. Discovered controlled C-H activation by photo-generated hydroxy radical from platinum(IV) hydroxo complexes. Hydroxo radicals are generally considered promiscuous reactants and our discovery suggests the possibility of controlled reactivity.

EARLY CAREER: Decoupling the Electronic and Geometric Parameters of Metal Nanocatalysts

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Funding: \$150,000 (2014)

PROGRAM SCOPE

It is a grand challenge to predictably control the geometric and electronic factors governing the performance of metal catalysts. Shape-controlled core@shell metal nanocrystals can address this challenge by providing independent control of these parameters through the binary composition and architecture. Shape-controlled nanocrystals express crystal facets with defined atomic arrangements, which are being exploited to achieve geometric control by selecting for specific interactions between adsorbates and a surface. These shape-controlled nanocrystals are then coupled with a core@shell architecture, where the core metal is anticipated to perturb the electronic structure of the shell metal as a function of shell thickness, providing a means of controlling the interaction strength between a molecular substrate and surface. Model systems have been identified and are being evaluated to establish that the geometric and electronic factors governing the performance of a metal catalyst can be independently controlled through the use of shape-controlled core@shell nanocrystals to achieve superior activity and/or selectivity. Concurrent with this study, new synthetic strategies to novel nanocatalysts including sub-10 nm shape-controlled core@shell nanocrystals, concave core@shell nanocrystals, and shape-controlled core@shell nanocrystals consisting of electropositive non-noble metal cores will be validated. Collectively, these experiments will establish shape-controlled core@shell nanocatalysts as transformative platforms toward efficient catalysis.

FY 2014 HIGHLIGHTS

To meet the research objectives of this grant, we undertook the first study in which the two main geometric parameters governing the performance of metal nanocatalysts – nanocrystal size and shape – were systematically decoupled. A series of size-controlled {100}-terminated Pd nanocubes and {111}-terminated Pd octahedra were studied as selective hydrogenation catalysts. The intrinsic catalytic activity of both Pd nanocubes and octahedra toward selective hydrogenation of 2-hexyne increased with increasing nanocrystal size and was attributed to an ensemble effect. We also found that the Pd octahedra were more active than Pd nanocubes, and this finding is consistent with previous reports that found alkynes bind more strongly to Pd(100) surfaces than Pd(111) surfaces, which can retard hydrogen binding and/or product desorption. These results are significant because they indicate that the geometric size effect can be decoupled from the geometric shape effect by keeping the nanocrystal shape constant and vice versa. These results were published in ACS Catalysis in 2014.

Nitrogen Atom Transfer From High Valent Iron Nitrides

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

Complexes containing the terminal iron nitrido unit can be stabilized with tripodal supporting ligands that enforce three-fold symmetry. However, the nitrogen atom transfer reactivity of these complexes tends to be modest and therefore new strategies are required to increase their reactivity. A key aspect of the electronic structure of three-fold symmetric tris(carbene)borate iron(IV) nitrido complexes is a low energy LUMO that is stabilized by Fe spd mixing. It is hypothesized that the energy of this orbital, and hence electrophilicity of the nitrido ligand, can be predictably tuned by changes to the supporting tripodal ligand. Specifically, changes to: (1) the donor strength, and (2) the bite angle of the supporting ligand, as well as (3) the oxidation state of iron, are expected to modify the electrophilicity of the nitrido ligand. These hypotheses will be tested by preparing iron nitrido complexes (in multiple oxidation states) supported by new tris(carbene)borate ligands that differ in their donor strength and bite angle, and investigating their reactivity in two-electron nitrogen atom transfer reactions. Reaction of the nitrido ligands with a series of substrates will be used to evaluate the impact of the supporting ligand on the thermodynamic propensity towards nitrogen atom transfer, as well as develop structure/activity relationships. Particular emphasis will be placed on nitrogen atom transfer to unsaturated hydrocarbons (e.g. alkenes, dienes), which combined with the development of methods for regeneration of the iron nitrido complexes, will lead to new cycles for the synthesis of nitrogen-containing heterocycles.

FY 2014 HIGHLIGHTS

A detailed investigation into the scope and mechanism of the reaction between the iron(IV) nitride and styrene, which yields an iron(II) aziridino complex, has been undertaken. These investigations reveal that the reaction occurs in a stepwise manner, likely by two one-electron steps that result in loss of stereochemistry. The reaction is faster with electron-poor styrenes and is also subject to steric

constraints. Intriguingly, the aziridination reaction is reversible, allowing for the first example of aziridine cross-metathesis. A functionalized aziridine can be liberated from the iron center, allowing for a synthetic cycle for aziridine cross-metathesis to be established. New, strongly donating bidentate ligands have been developed to isolate three-coordinate iron and cobalt complexes. While attempts to use bis(carbene)borate and tris(carbene)borate ligands to prepare iron alkylidenes and alkylidynes have been so far unsuccessful, one such ligand stabilizes an unusual paramagnetic isocarbonyl complex that has a formal iron(0) oxidation state. This reduced complex is reactive towards dihydrogen, and thus may provide a homogeneous model complex for the Fischer-Tropsch reaction. Efforts have also been made to prepare iron phosphido and sulfido complexes with tris(carbene)borate ligands. These investigations have led to the isolation of an η^3 -cycloP₃ complex which is unusual due to its triplet spin configuration. Attempts to prepare a sulfido complex have resulted in conversion of the carbene ligands being converted to thioimidazole donors.

Copper-Catalyzed Aerobic Oxidation of Arenes and Alcohols

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Funding: \$175,000 (2014)

PROGRAM SCOPE

Our DOE-sponsored research addresses two critical challenges in modern catalysis research: (1) replacing precious metals with earth-abundant elements as catalysts for chemical synthesis and energy-related applications and (2) controlling the reactivity of molecular oxygen in selective aerobic oxidation reactions. Numerous metalloenzymes feature first-row transition metals in their active sites, and an array of Cu- and Fe-containing enzymes mediate aerobic oxidation of organic molecules. In contrast, many of the recent synthetic advances in aerobic oxidation catalysis utilize noble metals, such as Pd, Rh. The development of new industrially useful catalyst systems derived from first-row transition metals remains a key challenge for the field. Our DOE-sponsored research efforts focus on the development and investigation of copper-catalyzed aerobic oxidation reactions. Although the systems of interest bear some resemblance to copper oxidase enzymes, the catalytic mechanisms that have emerged from these studies are more closely related to organometallic oxidation reactions catalyzed by noble-metal (e.g., Pd, Pt) catalyst systems. Our research has focused on the discovery and/or mechanistic characterization of two important classes of aerobic oxidation reactions catalyzed by homogeneous copper catalysts: (1) oxidative functionalization of arene C–H bonds and (2) chemoselective oxidation of primary alcohols.

FY 2014 HIGHLIGHTS

Research progress from our FY2014 DOE project included results from both of our two project areas: (1) investigation of Cu-catalyzed methods for aerobic oxidation of aromatic C–H bonds (one publication) and (2) development and mechanistic characterization of (bpy)Cu/TEMPO-catalyzed aerobic alcohol oxidation (six publications). Specific highlights included the following:

- A. Observed Divergence between Organometallic and Single-Electron-Transfer Mechanisms in Cu(I)-Mediated C–H Oxidation of a Single Substrate.

Key publication:

- Suess *et al.* 'Divergence between Organometallic and Single-Electron Transfer Mechanisms in Copper(II)-Mediated Aerobic C–H Oxidation.' *J. Am. Chem. Soc.* 2013, 135, 9797–9804.
- B. Development of Highly Efficient Methods for Aerobic Alcohol Oxidation and Characterization of their Reaction Mechanism.

Key publications:

- Steves & Stahl. 'Copper(I)/ABNO-Catalyzed Aerobic Alcohol Oxidation: Alleviating Steric and Electronic Constraints of Cu/TEMPO Catalyst Systems' *J. Am. Chem. Soc.* 2013, 135, 15742-15745.
- Greene *et al.* 'Continuous-Flow Aerobic Oxidation of Primary Alcohols with a Copper(I)/TEMPO Catalyst.' *Org. Process Res. Dev.* 2013, 17, 1247-1251.
- Ryland & Stahl. 'Practical Aerobic Oxidations of Alcohols and Amines with Homogeneous Cu/TEMPO and Related Catalyst Systems.' *Angew. Chem. Int. Ed.* 2014, 53, 8824-8838.
- Ryland *et al.* 'Mechanism of Alcohol Oxidation Mediated by Copper(II) and Nitroxyl Radicals.' *J. Am. Chem. Soc.* 2014, 136, 12166–12173.

Our work in the latter area was particularly noteworthy because some of the work was carried out in collaboration with three pharmaceutical companies in an effort to facilitate large-scale application of our methods. This work was recognized in October 2014 with the Presidential Green Chemistry Challenge Award (Academic category).

Institute for Catalysis in Energy Processes

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 Randall Snurr; Northwestern University
 Harold Kung; Northwestern University
 Richard Van Duyne; Northwestern University
 Eric Weitz; Northwestern University
 Students: 2 Postdoctoral Fellow(s), 10 Graduate(s), 0 Undergraduate(s)
 Funding: \$850,000 (2014)

PROGRAM SCOPE

The Institute for Catalysis in Energy Processes (ICEP) is a multi-investigator project in the Northwestern University Center for Catalysis and Surface Science (NU). It has strong connections to the catalysis research group at Argonne National Laboratory (ANL) through joint appointments of several PIs. The overarching theme of ICEP research is Chemical Catalysis: Manipulation and Understanding of Oxidation Catalysts. The objectives of the project are 1) Elucidate the structure-function relationships in oxidation catalysts of several forms, supported molecular oxides, supported metal nanoparticles, and supported metal atoms and 2) Understand the roles of different oxidizing species in catalytic oxidation.

Specific objectives for the project year have been 1) Develop the oxidation of cyclohexene as a versatile and informative probe reaction for oxidation pathways, 2) Develop the capability to carry out catalytic reaction experiments with a variety of oxidants: O₂, H₂O₂, NO, N₂O, organic hydroperoxides and begin reaction studies, 3) Synthesize and characterize new catalytic materials with novel structures designed to probe specific questions about structure-function relationships, and 4) Advance our characterization methodologies, both experimental and computational, to obtain an atomic scale picture of our catalytic materials and their function.

FY 2014 HIGHLIGHTS

Detailed studies using X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) combined with HRTEM examined the influence of SrTiO₃ termination on the structure and composition of supported, catalytic Pd nanoparticles prepared by ALD. On the SrO termination the average Pd particle size is 2-3 nm independent of the loading. On the TiO₂ termination the size increases with loading. The Pd particle composition shifts with increasing numbers of ALD cycles from oxide to metallic state. We successfully imaged the Ce and O atom positions on the different surfaces of CeO₂ nanoparticle supports by using the aberration-corrected high resolution electron microscopy (HREM). To study the direct participation of support atoms in the catalytic site responsible for selective propane oxidation by supported Au, well-defined Ti-containing ligands for the Au particles have been created that can serve as a surrogate of the metal-support interface. This approach was used to study how the presence of Ti species influences catalytic oxidation of propane. Using mononuclear Ti ligands only, acetone is formed. With dinuclear Ti ligands both acetone and propene are formed. Vanadium oxide monomer species were introduced into well-defined sites in a metal organic framework (MOF) structure. The resulting, molecularly well-defined species were active for the oxidative dehydrogenation of cyclohexene to benzene with a performance similar to conventional alumina-supported vanadia catalysts. Using SrTiO₃ as the support for vanadium oxide small amounts of cyclohexadiene were also observed for the first time. The interaction of supported vanadia species with a second surface cation, either W or Mo, was examined by x-ray standing wave measurements to better understand the behavior of complex, multicomponent catalysts. The presence of vanadia makes normally non-reducible W reducible by hydrogen under mild conditions.

Porous Transition Metal Oxides: Synthesis, Characterization, and Catalytic Activity

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Funding: \$145,000 (2014)

PROGRAM SCOPE

The goals of this project are to synthesize well-ordered crystalline mesoporous transition metal oxide (MTMO) materials with monomodal uniform pore sizes; to prepare and characterize ordered mesoporous thin films; to optimize catalytic activity, selectivity, and stability in oxidation catalysis using amorphous porous oxides and crystalline microporous and mesoporous materials; to investigate the role of mesoporous materials in battery systems; and to develop novel *in situ* characterization methods for syntheses, selective oxidations, and battery studies. The assembly of these materials involves

inverted micelles. Characterization of the nucleation process has been done with Fourier transform infrared spectroscopy. Morphological studies have been done with a combination of scanning and transmission electron microscopy methods. A unique feature of these MTMO materials is that various compositions can be prepared such as CoO, Co₃O₄ and other known structures of metal oxides. This in turn allows enhanced thermal stability of such materials that are most often made by preparations similar to MCM-41 or by replica methods, both of which are rather limiting. Various metal oxides of titanium, manganese, iron, cobalt, nickel, copper, zinc, zirconium, aluminum, silicon, tin, cerium, and many others have been made. Taking advantage of the control of pore size has led to enhanced activity in coupling reactions as well as oxidation reactions. The adsorptive properties of these materials are enhanced since the synthesis process allows numerous ordered pores greater in void volume than typical mesoporous materials. The primary focus of our work has been in understanding catalytic selective oxidation reactions of hydrocarbons with both microporous and mesoporous metal oxides. Details of reaction mechanisms are under investigation.

FY 2014 HIGHLIGHTS

This year we have successfully made uniform monomodal pore sized crystalline walled mesoporous metal oxides of various compositions and structures. In addition, metal sulfide, phosphated materials, sulfated materials, and mixed metal oxide systems have been made. These materials have been screened for adsorption of various sulfur and nitrogen poisons and catalytic activity. These materials have been expanded to systems throughout the periodic table that have outstanding thermal stabilities, physical, and chemical properties. In this last year we are focusing on the characterization of the mechanisms of formation of these materials, which are made of nano-size crystallites that align during synthesis and do not sinter. In addition, we are studying specific catalytic activity of these different systems and applications regarding adsorption, sensors, and battery materials. Optimization of properties and correlation of such properties to desired functions are being pursued. Highlights include a major publication in Nature and numerous invitations for presentations of the above materials. Unique magnetic, optical, structural, porous, electronic, and other properties have been realized.

Polynuclear Aromatic Hydrocarbons with Curved Surfaces: Buckybowls

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Funding: \$140,000 (2014)

PROGRAM SCOPE

This program deals with the synthesis, structural studies, and chemistry of curved-surface, polynuclear aromatic hydrocarbons (PAHs) with carbon frameworks structurally related to fullerenes. They are referred to as “buckybowls” or “fullerene fragments”. Previous work under this DOE sponsored program produced several new buckybowls and, more importantly, resulted in a development of efficient, gram-scale solution synthetic methodologies for preparation of small buckybowls, most notably corannulene (C₂₀H₁₀) and its derivatives. During this funding cycle we plan to employ the corannulene-based synthons previously developed in our laboratory to prepare a number of highly nonplanar molecular architectures with two or more corannulene subunits. This “bottom-up” approach will produce well

defined carbon-rich systems of nanometric scale which, besides their “pure chemistry” value will have a potential for applications as novel materials in separation sciences, nanoelectronics, photovoltaics and catalysis. We have two broader objectives for the cycle: Synthesis of Bowl Shaped Systems of Nanometric Dimensions: Utilizing the palladium-catalyzed cyclotrimerization reaction of 1,2-didehydrocorannulene and Diels-Alder cycloaddition methodology we will prepare a number of large, highly nonplanar systems with multiple corannulene subunits. Molecular Receptors with Corannulene Pincers: As we showed recently “molecular clips” with corannulene pincers can act as molecular receptors for fullerenes, binding through $\pi-\pi$ convex-concave stacking of the curved conjugated carbon networks. We propose a preparation and testing of a number of new molecular receptors with two or more corannulene clips with improved affinity and specificity toward guest molecules, including fullerenes. An integrated approach to the design of efficient clips will lead to molecular receptors for fullerenes which are even more efficient than “buckycatcher”, prepared recently in our laboratory.

FY 2014 HIGHLIGHTS

We have initiated rigorous studies of thermodynamics of host-guest association of molecular clips and tweezers in organic solvents. In addition to ^1H NMR titration experiment we probed the thermodynamics of association employing Isothermal Calorimetry (ITC). [J. Phys. Chem. B, 2014, 118, 11956]. The results show that thermodynamics of the host-guest complex formation in solutions is more complicated than expected and proposed by the existing computational models. ITC experiment proves that $-\Delta S$ values for the association are generally either negligibly small or even negative, in contrast with the strongly positive values predicted by the available computational models. In addition, our study demonstrates the significant reductions of the association constants resulting from switching solvents, the changes which are not predicted the solvation model. A series of inclusion complexes and/or solvates of buckycatcher were characterized by the X-ray diffraction study, demonstrating a remarkable versatility of the clip to accommodate guest molecules of various sizes and shapes. [Cryst. Growth Des. 2014, 14, 2633]. Dramatic variations of the intercentroid distances between the central five-membered rings of the corannulene pincers (from 7.87 to 11.51 Å) in the inclusion complexes expose an impressive flexibility of the buckycatcher tether. The unprecedented concave-convex conformations of buckycatcher were found in two of the studied solvates. An x-ray structure of the crystal of buckycatcher grown by high-vacuum sublimation (i.e. in the absence of solvents) in Marina Petrukhina laboratory showed that the clip “grabs itself” if it does not have any proper guest molecules around. [Chem. Commun. 2014, 50, 2657]. The generation and X-ray structure of the dianionic form of buckycatcher (with two Ru counteractions) was also achieved by collaboration with Petrukhina. The first report characterizing the buckycatcher dianionic state was highlighted in the RSC blog Chemistry World.

Metal/Organic Surface Catalyst for Low-Temperature Methane Oxidation: Bi-Functional Union of Metal-Organic Complex and Chemically Complementary Surfaces

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Funding:	\$150,000 (2014)

PROGRAM SCOPE

Pressing energy challenges require new innovations in the development of catalyst systems that bridge the capabilities of two traditionally distinct fields of catalysis: homogeneous and heterogeneous catalysis. Homogeneous catalysis has key advantages in the design of well-defined single-site metal centers to achieve high selectivity in reactions. Heterogeneous catalysts generally have high activities and are developed with greater thermal stability. Bridging these fields will open new opportunities in energy science and technology. Catalysis research is a critical component of the solution portfolio to our energy challenges, but requires new advances in developing high activity and high selectivity in key energy processes. This project explores new possibilities in catalysis by combining features of homogeneous catalysts with those of heterogeneous catalysts to develop new, bi-functional systems. We are studying the interactions of metal–organic catalysts with surface supports and their interactions with reactants to enable the catalysis of critical hydrocarbon reactions at lower temperatures. These systems consist of metal–organic complexes that form by redox assembly at solid surfaces to produce well-defined single-site metal centers in a uniform oxidation state. The tunability of these systems will allow a high degree of control over the surface chemistry. This work addresses fundamental chemistry problems in these systems. What are the essential ingredients for highly-ordered and well-defined single-site metal centers? How do the metal–organic complexes interact with the surface? Can those metal center sites be tuned for selectivity and activity as they are in the homogeneous system by ligand design? Study of these systems brings together the advantages of heterogeneous catalysis with those of homogeneous catalysis, and takes this a step further by pursuing the objective of a bi-functional system.

FY 2014 HIGHLIGHTS

The central hypothesis of the FY 2014 period was that single-site transition metal complexes could be formed by on-surface redox chemistry with appropriate ligands at a metal surface. We have experimented with different methods to achieve single-site metal center stabilization at the surface, specifically, multiple organic ligand coordination environments for Pt metal centers on a surface support. Design of ligands for effective Pt complexation at surfaces was pursued with two key design principles in mind: effect metal coordination by electron accepting ligand and bidentate coordination site with a diverging geometry to allow attachment of ligand on both sides of the molecule. These design principles led to a highly successful ligand, dipyridyl tetrazine, a redox-active sub-unit to enable charge transfer within the adsorbate layer, i.e., redox-assembly at the surface. We have discovered the formation of single-site Pt(II) centers within coordination chains on a reconstructed Au(100) surface. We demonstrated that these redox-assembled chains are stable to 150°C, bringing them into a temperature range of high interest for moderate temperature reactions. They also serve as easily tuned model systems for exploring the chemistry of single-site transition metals that hold potential for future applications in tandem catalysts and development into a zeolite or other highly-stable support structure. This system is one of several that have been developed in the exploration of metal coordination at surfaces that allow us to better understand the synthesis and the chemical activity of these systems with the goal to develop a highly-selective and tunable surface catalyst by metal–organic complexation at the gas/solid interface. We have also identified key questions for ongoing research, including exploration of mixed valence systems, ligand designs for efficient assembly, chemical activity and selectivity, and extension of these results to other catalysis systems.

Understanding the Catalysis on Early Transition Metal Oxides-Based Catalysts Through Exploration of Surface Structure & Chemistry During Catalysis Using in-situ Approaches

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PROGRAM SCOPE

The current DOE project explores phase transformation, the accompanying changes of surface chemistry, and their impacts on catalytic activity and selectivity for reduction of nitric oxide and water gas shift (WGS). Our work to date has shown the complexity of surface chemistry of early transition metal oxide-based catalysts, the flexibility of oxide surfaces in restructuring a surface phase to tune catalytic performance, and the possibility of development of new catalytic phases through phase transformation under reaction conditions. We developed nonstoichiometric CoO_{1-x} nanorod catalyst which exhibits 100% selectivity for production of N_2 from NO with high activity at 250°C . Through a surface restructuring during catalysis, $\text{Pt}_1\text{Co}_n/\text{Co}_3\text{O}_4$ and $\text{Pd}_1\text{Co}_n/\text{Co}_3\text{O}_4$ catalysts were formed. They exhibit high activity in the reduction of nitric oxide with H_2 . In addition, new phase $\text{Pt}_m\text{Co}_n/\text{CoO}_{1-x}$ with high activity in WGS was developed by restructuring $\text{Pt}_1/\text{Co}_3\text{O}_4$ catalytic surface under a WGS condition. We have also developed oxide-based catalysts for other conversion of methane and other reactions.

FY 2014 HIGHLIGHTS

We have performed the following work: (1) in-situ studies of surface chemistry of Co_3O_4 and Co_3O_4^- based catalyst during water gas-shift and design of a new bi-functional catalyst, Pt-Co alloy nanoclusters supported on nonstoichiometric CoO_{1-x} bimetallic catalysts; (2) preparation and in-situ studies of Co-Ru bimetallic layers on Co_3O_4 nanorods for reduction of CO_2 ; (3) catalysis and in-situ studies of CeO_2 with doped metal cations for generation of syngas through partial oxidation of CH_4 ; (4) catalysis and in-situ studies of reduction of NO with CO on nonstoichiometric CoO_{1-x} ; (4) catalysis and in-situ studies of water-gas shift on mesoporous CeO_2 loaded with metal nanoclusters consisting curvy metal-oxide interface; (6) chemical transformation of methane to methanol⁹ and acetic acid¹⁰ through oxidation in solutions, (7) in-situ studies of surface oxide, $\text{Rh}(110)\text{-}1\times 2\text{-O}$ at atomic scale during CO oxidation.

Catalysis of Small Molecule Activation By Proton Coupled Electron Transfer

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PROGRAM SCOPE

The objective of this project is the catalysis of 'proton coupled electron transfer' (PCET) to metal bound fragments derived from the most abundant small molecules (i. e. O₂ and N₂). There are many important chemical challenges that are tied to this fundamental reaction. Among these are: i) metal catalyzed oxidations of organic molecules utilizing O₂ as the oxidant ii) reduction of O₂ to water close to the thermodynamic potential – in other words, the cathode of any fuel cell based on reactions with O₂ iii) transfer of reduced nitrogen species to organic substrates iv) fixation of nitrogen at modest temperatures and pressures The realization that 'hydrogen atom abstraction', i. e. an elementary step occurring e. g. during the course of metal-catalyzed hydroxylations or aminations, must be considered a PCET process brings into focus the broader issue of the synchronous delivery of protons and electrons to metal bound atoms and molecules. The conceptual separation of H⁺ and e⁻ and their respective sources and destinations leads directly to a consideration of redox-active ligands, and the role they might play in facilitating PCET processes. One of the facets of the proposed research is to create metal complexes with redox-active functional groups, and thereby functionally mimicking metalloenzymes with electron transfer sites. The methods employed involve the synthesis and characterization of coordination compounds of various transition metal (Cr, Mn, Fe, Co) as well as the study of their reaction mechanisms. Diversity in coordination geometries will create opportunities for new chemistry. Redox-active versions of these ligands will facilitate PCET processes. Benefits of this research include the potential discovery of new catalytic processes and the advancement of fundamental knowledge about chemistry and catalysis.

FY 2014 HIGHLIGHTS

1) We have prepared a series of ferrocenyl substituted tris(pyrazolyl)borate ligands, including the Tp(Fc,Me) ligand (Inorg. Chem. 2014, 53, 9424). Various transition metal complexes of the latter ligand have been prepared. The reactivity of such complexes, particularly vis-a-vis the resistance of the ligand to H-atom abstraction and its redox activity are currently being explored. 2) We have continued the investigation of the chemistry of TpCo(I) and TpFe(I) dinitrogen complexes, with particular regard to the activation of dioxygen and other small molecules. Imido complexes of this metal fragment continue to play an important role in our work. 3) We have investigated - experimentally as well as computationally - the apparent 4-electron oxidative addition of O₂ to a low-valent NacnacCr(I) fragment, which results in the formation of a Cr(V) dioxo complex. This reaction is spin-forbidden, and we have found that the minimum energy crossing point (MECP) between the two potential energy surfaces (PES) is of relatively high energy. Accordingly, a more complicated mechanism, involving the formation of a dinuclear chromium intermediate, appears to be operative (JACS 2013, 135, 16774).

EARLY CAREER: Early-Late Heterobimetallic Complexes Linked by Phosphinoamide Ligands: Tuning Redox Potentials and Small Molecule Activation

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Funding: \$150,000 (2014)

PROGRAM SCOPE

The goal of this project is to investigate bimetallic combinations of early and late transition metals linked by phosphinoamide ligands. We have previously found that the interaction of an electron-withdrawing Zr center can decrease the electron density at a Co center to such an extent that the complex's reduction potential is increased by as much as 1 V compared to monometallic Co analogues. We aim to investigate whether this phenomenon is true for an array of early/late heterobimetallic combinations, and whether the ability to tune redox potentials via metal-metal donor-acceptor interactions may provide a method to perform small molecule activation and catalysis with decreased overpotentials. While early/late heterobimetallic complexes may find a variety of applications in catalysis, we are particularly focused on their application towards the activation of strong sigma-bonds in small molecule substrates such as carbon dioxide.

FY 2014 HIGHLIGHTS

A number of independent areas were explored to address the overall goals of the project. To explore the mechanism of carbon dioxide activation by Zr/Co complexes, we used a series of control experiments as well as some fundamental studies of C=O bond activation using ketone substrates to better understand the unique mechanism of carbon dioxide activation. In particular, we explored the unique role that Zr and Co play in these reactions and the cooperativity between the two metals that inevitably leads to reactivity that would not be possible with a single metal center. We have found that a single-electron pathway involving initial coordination to the Zr center may be operative, but that the key step in the cleavage of a C=O bond involves coordination of the substrate (CO₂) to both Zr and Co. We have also investigated the reactivity of other small molecule substrates with reduced Zr/Co heterobimetallic complexes and, among other discoveries, uncovered a four-electron redox process by which N=N double bonds are cleaved. The role of the phosphinoamide ligands that link Zr and Co has been assessed by several studies involving variation of the ligand substituents, using the IR stretches of metal-bound carbonyls and differences in reactivity and redox properties as probes. While the Zr/Co heterobimetallic system we have studied has led to some unprecedented reactivity and some important fundamental insight into the cooperative roles of two metals in a bimetallic system, we have concluded that this system is hindered by the strength of the metal-heteroatom bonds that are formed with the Zr center as a result of sigma and pi bond cleavage reactions. Thus, we have investigated new metal-metal combinations, including homobimetallic complexes in which the two metals are distinguished only by the different donors in the two coordination sites available, including Cr/M (M = Fe, Co, Cu, Ir, Rh), Ti/M (M = Fe, Co, Ni), and Co₂ complexes.

In-Situ NMR/IR/RAMAN and *Ab Initio* DFT Investigations of Pt-Based Mono- & Bi-Metallic Nanoscale Electro-Catalysts: From Sulfur-Poisoning to Polymer Promoters to Surface Activity Indexes

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PROGRAM SCOPE

While continue to focus on the surface chemistry of sulfur (S) and other conventional poisonous species on Pt-based electrocatalysts, we are exploring a novel perspective of it, which was inspired by some very

interesting previous observations. Specifically, it was observed that the traditionally undesirable species can actually promote, rather than poison, catalytic activity of Pt-based electrocatalysts. This includes that (1) at <20% low coverage, adsorbed S species can promote considerably CO oxidation reaction (COR), methanol oxidation reaction (MOR), and oxygen reduction reaction (ORR); (2) adsorbed PVP can enhance substantially MOR and formic acid oxidation reaction (FAOR); and (3) adsorbed iodine can improve significantly the stability of PtCu alloy electrocatalyst for ORR. These observations are along the line of a new emerging area of research in which many traditional poisoning species have been observed to promote catalytic reactions. However, much of the surface chemistry that governs such behaviors remains to be uncovered and their potential practical applications are largely unexplored. Therefore, we are pursuing two primary objectives: 1. Advance significantly our fundamental understanding of the surface chemistry that governs the observed promotion in catalytic activity by some traditionally poisonous species (sulfur, PVP, and iodine) on Pt-based electrocatalysts through meticulous *in situ* spectroelectrochemical (NMR/IR/Raman) interrogations of the relevant systems. 2. Identify, Investigate, and establish correlations between the chemical descriptors of activity, such as the surface d band center or/and reactivity indexes and the associated electrochemical reactivity. An important aspect is that the activity indexes defined within the DFT framework are directly related to the surface local density of states at the Fermi level which are measurable by *in situ* electrochemical (EC)-NMR and calculable by the state-of-the-art *ab initio* DFT calculations

FY 2014 HIGHLIGHTS

1. Study of the PVP effect.

- a. By using a liquid phase UV photo-oxidation technique, we were able to eliminate the tenacious PVP off the octahedral/tetrahedral (O/T) and cubic Pt NPs. This enabled us to separate the NP surface orientation from the PVP effect. We observed that the MOR activity was enhanced by the O/T Pt NPs compared to Pt black and the cubic Pt NPs. The *in situ* ATR-SEIRAS data strongly suggests that the enhancement in MOR was probably related to more weakly hydrogen-bound water available on the O/T NP surface than on the other two samples (RSC Adv. 2014, 4, 21284).
 - b. We carried out more detailed EC and IR study of MOR and COR on the cubic and O/T Pt NPs with residual PVP. While our data confirmed the enhanced MOR activity on the O/T Pt NPs observed previously, the *in situ* IR data of much higher quality provided strong indications that the underlying reason for the MOR enhancement on the O/T Pt NPs was highly likely related to the enhanced no-CO-generating reaction pathway(s), as evidenced by much lower CO generation during the MOR on these Pt NPs (Electrocatal. 2014, 5, 248).
2. On the chemistry of activation of PtRu NPs for the MOR. While potential cycling has been widely used to activate PtRu NPs for MOR, little is known about the chemistry and what constitutes the optimal activation. *In situ* ATR-SEIRAS study of the activation–deactivation process in PtRu/C, which was corroborated by TEM, EDS, and XRD data, revealed that the commonly used catalyst activation procedure caused a dynamic redistribution of surface Pt and Ru that moved the catalyst surface from the initial alloyed distribution of Pt and Ru to more segregated distributions of each element. The best activation corresponded to achieving an equal amount of segregated surface Pt and Ru ensembles, presumably to maximize the Pt–Ru boundaries. However, over-activation led to the deactivation of the catalyst, largely caused by the substantial loss of surface Ru (Chem Commun 2014, 50, 12963)

Molecular-Level Design of Heterogeneous Chiral Catalysts

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Funding: \$650,000 (2014)

PROGRAM SCOPE

The goal of this project by the Chiral Catalysis Group is to understand the interactions of prochiral reactants or chiral products on chirally modified surfaces that lead to the preferential formation of one enantiomer over the other, with the goal of understanding the principles that govern the operation of heterogeneous chiral catalysts. While catalysis research has focused on improving activity, the focus has shifted to improving the selectivity or the atom efficiency of catalytic processes. Enantioselectivity, the ability of a catalyst to select between the two enantiomers of a chiral product, is one of the subtler forms of selectivity and is one of the most challenging problems in chemistry because it seeks to discriminate between two enantiomeric products that are identical in all respects except for their mirror reflection symmetry. Enantioselectivity is also central to catalytic processes that are at the heart of the pharmaceutical and agrochemical industries. The research focuses on three types of enantiospecific interactions of chiral molecules with chiral catalytic surfaces: interactions with naturally chiral surfaces; interactions with chirally templated surfaces; and one-to-one interactions of prochiral molecules with chiral surface modifiers. The specific goals are to: determine the structures of chiral surfaces, prochiral reactants, chiral products and chiral modifiers; understand the enantiospecific interactions that occur between prochiral reactants and chiral products with chirally modified surfaces; develop methods for detection of enantiospecific surface phenomena; elucidate enantioselective reaction pathways and the effects and interactions that control them; and develop novel chiral catalytic materials. The range of expertise within the Chiral Catalysis Group includes molecular-scale theory, surface science experiments in vacuum and under more-realistic liquid- and gas-phase environments, materials synthesis, and catalytic measurements.

FY 2014 HIGHLIGHTS

1. Measured enantiospecific adsorption equilibria for amino acids on chiral Cu(3,1,17)^{R&S} demonstrating enantiomeric separation on a naturally chiral surface.
2. Observed adsorption-induced auto-amplification of enantiomeric excess of aspartic acid (Asp) on Cu(111).
3. Demonstrated that D- and L-Asp mixtures undergo steady-state catalytic decomposition on Cu(111) and Cu(643)^{R&S}.
4. Used XPS to map rates of tartaric acid (TA) and Asp decomposition on a Cu(111) structure spread single crystals.
5. Quantified enantiospecific adsorption of propylene oxide and propranolol on chirally modified, tetrahexahedral (24-sided) Au nanoparticles.
6. Identified differences in adsorption of enantiopure versus mixed-enantiomer propylene oxide (PO) on Pt(111), explained by a kinetic effect analyzed using Monte Carlo simulations to model kinetic and STM data.
7. Demonstrated that NEA adsorption on Pt in a CCl₄ solution is dominated by interactions with the amine, not via the aromatic ring as commonly believed.

8. Correlated cinchona adsorption with catalytic activity for alpha-keto ester hydrogenation, influenced by concentration, nature of the solvent, and dissolved gases.
9. Demonstrated that the chemistry of tethered chiral modifiers is affected by the non-selective catalytic activity of the oxide surface, the activity of the OH species generated by hydrolysis of Si-alkoxy groups, and the tethered chiral modifier.
10. Demonstrated the use of glycidol as a chiral probe on Pd(111).
11. Characterized the surface chemistry of TA on Pd(111) showing that TA on Pd(111) is not a chiral modifier for PO but is for glycidol, due to the hydrogen-bonding interactions with $\bar{\text{O}}\text{H}$ groups on glycidol and TA.
12. Identified the tetramers and dimer rows formed from alanine (Ala) on Pd(111) and demonstrated that the amino acid tetramer forms chiral templates.
13. Identified docking complexes between MP and NEA on Pd(111) showing preferential enol binding accounting for enhanced MP hydrogenation.

Development of Catalytic Alkylation and Fluoroalkylation Methods

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 Funding: \$155,000 (2014)

PROGRAM SCOPE

The objectives of this project are to understand at the molecular level the details of metal-mediated transformations involving alkanes and fluoroalkanes so that better alkylation/fluoroalkylation methods and reagents may be developed. The proposed research focuses on using cheap, readily available, and environmentally benign metals in efforts to overcome certain obstacles and to make the new methods as universal as possible. The alkyl-alkyl cross-coupling methodology we are developing can help understand how to convert natural gas feedstocks to useful chemicals. Fluorination has become popular for its known ability to increase the oxidative and thermal stability of new materials, and its role in supporting new energy technologies is expected to grow. Also of growing importance are the applications of fluorination reactions and various fluorides to energy conversion materials for lithium batteries, fuel cells, solar cells, etc. Fluoroalkyl groups are known to be one of the most challenging fluorine-containing functional groups to manipulate synthetically, and understanding how to control their reactivity can lead to better methods to prepare a diverse array of products such as fluorinated refrigerants, surfactants, polymers, liquid crystals, aerosol formulations, and lubricants. Controlling additions and eliminations of fluoroalkyl groups are also expected to lead to new “greener” ways to prepare high-performance fluoroalkyl polymers and coatings that do not rely on the chemistry of fluoroalkenes, which are becoming increasingly unavailable to purchase due to the explosion hazards associated with their handling. Such polymers are of high value because they are chemically inert and stable at extreme temperatures. Fluoropolymers can also be used as oxidizers in metal-based pyrolant designs for the preparation of energetic materials, owing to the favorable enthalpy of formation of the metal-fluorine bond.

FY 2014 HIGHLIGHTS

For the fiscal year 2014, we have developed new synthetic routes to zinc-based perfluoroalkyl dinucleophiles that could be used in a variety of chemical transformations of interest to the Department of Energy such as perfluoroalkyl co-polymerizations, metathesis-like reactions, and cross-coupling reactions. Traditionally, these types of perfluoroalkyl nucleophiles prepared have problematic issues associated with their use. For instance, the related di-Grignard reagents must be used at low temperatures because they have a half-life of only two hours at -50 degrees Celsius in THF. We observed that 87 percent of our dizinc reagents persist in acetonitrile solution after 300 hours at room temperature. The dizinc reagents we have developed are operationally simple to prepare using inexpensive and easy to handle zinc metal. The zinc reagents are also critical for preparing new types of high-valent nickel complexes, which are key targets for developing alkylation and perfluoroalkylation reactions. The difficult step in metal-mediated perfluoroalkylations is the reductive elimination of R-Rf. We have prepared a Ni(III) fluoroalkyl species in order to obtain the first structure/reactivity parameters that will help us understand how to facilitate reductive eliminations at nickel. This complex has been structurally and spectroscopically characterized, and represents the first example of a well-defined paramagnetic fluoroalkyl complex of nickel. The complex is a key find because in order to understand how to use the more naturally abundant first-row metals in catalysis, a more detailed knowledge of the reactivity patterns of the less-commonly studied paramagnetic redox states is required. Cyclic voltammetry studies also suggest that the rarely seen Ni(IV) redox state is also accessible.

Surface Science Studies of Nano-Crystalline Metal Oxide and Metal-Metal Oxide Core-Shell Catalysts

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PROGRAM SCOPE

In this project we are attempting to bridge the materials gap between fundamental surface science studies of metal-oxide, single-crystal model catalysts, and high surface catalysts that are used industrially by measuring structure-activity relationships for thin films of well defined, metal oxide nanoparticles. The research program is concentrating on systems that are of interest for use as catalysts for complete-, selective- and photo-oxidation of organic oxygenates and builds upon our group's extensive experience in using surface-sensitive spectroscopic techniques to elucidate structure-activity relationships for oxide surfaces. The goals of this work are (1) to determine the role that highly undercoordinated edge and corner sites play in catalysis on oxides, (2) determine if control of oxide nano-crystalline size and shape can be used to design highly active and selective catalysts for specific reactions, and (3) determine how crystallite size and shape affect the photocatalytic properties of semiconducting oxides such as TiO₂. In addition to studies of nanocrystalline oxides, the research program will also include studies of hierarchal structured core-shell materials in which a metal nanoparticle is encased in a porous nano-crystalline oxide shell. Such materials have interesting catalytic properties and our goal in this work will be to use these unique model systems to study synergistic interactions between a metal and a reducible metal oxide support.

FY 2014 HIGHLIGHTS

Research during the 2014 focused on exploring structure-activity relationship for small organic oxygenates on catalytic titanium dioxide anatase nanocrystals. Methanol, ethanol, acetaldehyde, and acetic acid were used as probe reactants. Experiments were conducted across a range of reactant coverages, nanocrystal geometries and sizes, and photochemical conditions. These studies have provided new insight into the active sites for specific reactions and how the densities of these sites can be controlled by crystallite size and shape. Methanol reactivity studies provide a good example of the types of insight we have obtained. The thermally induced reaction of methanol on anatase TiO₂ nanocrystals produces primarily dimethylether and by comparison to what has been reported in previous in studies using macroscopic single crystals and powders we have been able to determine that this coupling reaction must either take place on (001) surfaces which are exposed in the nanocrystals or at edge sites. In contrast for the photochemically-induced oxidative coupling of methanol to produce methyl formate, (101) anatase surface planes have been identified as the active surface. Our studies have also provided new insight into the mechanisms of photochemical reactions on TiO₂. For the photochemical reaction of methanol to methyl formate it was observed that the methyl formate production increased at the expense of dimethylether production with increasing UV photon flux thereby demonstrating the central role of adsorbed methoxide groups in the photochemical reaction and that this reaction also occurs on the exposed (101) planes. The fact that the overall reactivity for the photochemical reaction was found to be independent of nanocrystallite size also supports this latter conclusion. Interestingly, size effects have been observed for the bimolecular ketonization of acetic acid, suggesting that edge in corner sites may be required for this reaction.

Theoretically Relating the Surface Composition of Pt Alloys to Their Performance as the Electrocatalysts of Low-Temperature Fuel Cells

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PROGRAM SCOPE

The main objective of this project is to gain fundamental knowledge about the relation between surface composition and catalytic performance of Pt alloy catalysts for electro-chemical reactions relevant to renewable energy technology.

Specific objective 1: Develop and improve a first-principles based multiscale computation approach to predict equilibrium surface composition of Pt alloy surfaces.

Specific objective 2: Evaluate the surface electronic structure and catalytic activity of Pt alloy catalysts.

Specific objective 3: Relate the surface composition and surface structure to the catalytic performance of Pt alloy catalysts.

FY 2014 HIGHLIGHTS

The project was launched on September 15, 2009. The research progress in this year includes the first-principles density functional theory (DFT) study of reaction energies and reaction mechanisms for

oxygen reduction reaction on Pt-based alloys and strained Pt surfaces as well as adsorption free energy of chemical species involved in methanol oxidation reaction on Pt-base alloys. The significant research achievements are: (a) our DFT results suggest that both ligand effect (subsurface transition metal such as Fe, Ni, and V) and strain effect (-2 to -3 % compressive strain) could lead to enhanced catalytic activity for ORR on surface-segregated Pt alloy catalysts as compared to pure Pt surface, and (b) the Pt/Co(111) surface, which was predicted to have the lowest onset potential in indirect pathways among the four Pt-based catalysts studied, could be a promising catalyst for CH₃OH oxidation to form CO₂. At this moment of the project, fifteen journal articles have been published from this grant.

Enabling Catalytic Strategies for Biomass Conversion

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Funding: \$380,000 (2014-2016)

PROGRAM SCOPE

The goal of the proposed research is to investigate the fundamental science related to the development of selective catalytic processes for converting renewable bio-feedstocks into new classes of value-added chemicals and thermoplastics. We have discovered a cationic Pd catalyst ligated by neocuproine (2,9-dimethylphenanthroline) that catalyzes the selective oxidation of glycerol to dihydroxyacetone, the selective oxidation of sugar-derived polyols to alpha-hydroxyketones, and the oxidative carbonylation of diols to cyclic carbonates. Investigations into the fundamental chemistry of the selective oxidation of glycerol has both illuminated some key insights on the origin of high selectivities of this reaction and opened up new opportunities for the selective catalytic oxidations of biomass-derived polyols. Specific objectives for the proposed work are to: (1) Investigate the basic science and mechanistic origin of selective catalytic oxidation reactions, particularly of biomass-derived polyols and carbohydrates; (2) Expand the scope of selective catalytic oxidation reactions for the synthesis of new renewable monomers and polymers and (3) Develop integrated catalytic strategies for conversion of biomass wastes to useful chemical intermediates and polymers. This research program embraces a mix of fundamental investigations of catalytic reactivity with targeted approaches for the catalytic synthesis of monomers and renewable polymers. We are investigating the mechanisms of selective aerobic oxidation of polyols and carbohydrates with Pd catalysts with a special focus on the role of hydrogen peroxide and peroxy intermediates in an effort to increase catalyst lifetime. We have also extended our studies on the selective oxidation of sugars to ketoses and the oxidative lactonization of 1,5-diols to generate new families of lactone monomers.

FY 2014 HIGHLIGHTS

Kinetic and mechanistic studies of the aerobic oxidation of alcohols with cationic (neocuproine)Pd catalysts led to the identification and characterization of a novel trinuclear Pd oxo complex, which was shown to be a competent catalyst precursor for alcohol oxidation. The formation of this complex implicates a new mechanism for the activation of oxygen by reduced Pd species. Recent studies of this complex implicate its role in the disproportionation of hydrogen peroxide, a key reactive intermediate that is responsible for the oxidative degradation of the catalyst. These studies led to the development of

sacrificial phenol additives that increased the catalyst lifetime and provided experimental protocols for aerobic oxidations with high turnover numbers at much lower Pd loadings. The scope of the Pd-catalyzed alcohol oxidations were extended to the oxidative lactonization of substituted diethanolamines to generate new families of morpholinones (aza lactones), which have used as monomers to generate highly functionalized degradable polyesters. The scope of selective oxidations with these Pd catalysts were also extended to carbohydrates, specifically the 6-carbon glucopyranosides and deoxy fucopyranosides as well as the 5-carbon ribopyranosides. In some cases, the catalytic oxidation of these sugars occurs selectively at the 3-hydroxyl position to generate 3-keto sugars. Significantly, these selective oxidations of sugars can be carried out in the absence of protecting groups in aqueous solution or mixed organic/aqueous media. The origin of the high selectivities of these oxidation reactions are a subject of ongoing investigations.

Alkane Activation and Oxidation on Pd-Pt Oxide Surfaces

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Funding: \$200,000 (2014)

PROGRAM SCOPE

Surface chemical reactions on Pd and Pt oxides play a central role in catalytic applications under oxygen-rich conditions, including the catalytic combustion of methane, the remediation of exhaust gases from automobiles and power plants and fuel cell catalysis. Unfortunately, however, difficulties in oxidizing Pd and Pt surfaces in ultrahigh vacuum (UHV) have limited the fundamental understanding of the properties and surface chemistry of Pd and Pt oxide phases. In this project, we are performing experimental and molecular modeling investigations of the growth and chemical reactivity of oxide phases generated on crystalline Pt and Pd surfaces in UHV using oxygen atom beams. We have been focusing particularly on characterizing the mechanisms governing the activation and oxidation of alkanes on pure and Pt-modified PdO(101) thin films. This focus is motivated by our discovery that alkanes adsorb as strongly-bound sigma-complexes on PdO(101) and that the sigma-complexes serve as precursors for facile C-H bond activation. The major goals of our work are to elucidate atomic-level steps involved in the oxidation of alkanes and CO on Pd oxide surfaces, and to develop microscopic models that can ultimately be used to predict reaction rates under practical conditions.

FY 2014 HIGHLIGHTS

During the 2014 period, we investigated the steady-state oxidation of methane on Pd(100) using ambient-pressure X-ray photoelectron spectroscopy (AP-XPS). This work shows that the formation of a multilayer PdO(101) film coincides with enhanced catalytic activity toward the complete oxidation of methane, whereas single layer PdO(101) is relatively unreactive. The high activity of the multilayer PdO(101) film observed under ambient pressure conditions agrees well with our prior UHV studies of alkane activation on this surface. Quantum chemical calculations reveal that multiple layer PdO(101) films are more reactive toward methane C-H bond cleavage than single PdO(101) layers due to electronic differences induced by the subsurface bonding partner. The effect that we discovered is analogous to ligand effects in organometallic complexes, and may be broadly applicable to

understanding the surface chemical properties of thin-film oxides. We also extensively investigated the oxidation of CO on Pd oxide phases using surface vibrational spectroscopy and density functional theory (DFT) calculations. Our results provide detailed insights into the mechanisms for CO oxidation on PdO(101), and reveal that surface oxygen vacancies created during reaction serve to promote further oxidation of CO. Additionally, our work shows that surface oxygen atoms are rapidly replenished by the bulk oxygen reservoir during CO oxidation at temperatures as low as 400 K, demonstrating a dynamic coupling between the creation and annihilation of surface oxygen vacancies during reaction.

Design and Characterization of Novel Photocatalysts with Core-Shell Nanostructures

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Funding: \$250,000 (2014)

PROGRAM SCOPE

The overall goal of this project has been to develop new a new and novel class of well characterized nanostructured Metal@TiO₂ core-shell and yolk-shell photocatalysts to address two fundamental issues presently limiting this field: (1) the fast recombination of electron-hole pairs once generated by light absorption, and (2) the recombination of H₂ and O₂ on the metal surface once produced. These model samples are also used to study the fundamentals of the photocatalytic processes. The specific objectives for this year have been to continue in our advances toward the three directions assigned to the three main members of the group. From a synthetic point of view, we continue to look for improved ways to make core-shell and yolk-shell materials with control on their key structural parameters. In terms of the characterization of the samples, the mass transport of the cells continues to be measured under realistic photocatalytic conditions, namely, in liquid phase by using infrared absorption spectroscopy. Finally, the photophysical behavior is being mapped out by using time-resolved measurements of transient light absorption and fluorescence and also the evolution of plasmon resonances over time, and correlated with photochemical activity. Correlations are being sought between those properties and structural parameters within the nanostructured samples.

FY 2014 HIGHLIGHTS

In terms of synthesis, we have made advances in several fronts: (1) we further improved our protocol for metal/TiO₂ core/shell composite nanostructures. A controlled sol-gel process has been recently developed to directly coat gold nanoparticles with a relatively thin layer of TiO₂ to produce Au@TiO₂ core-shell catalyst particles, which can be rendered crystalline via calcination at high temperatures. (2) The synthetic strategy for hollow TiO₂ shells has been extended to other catalytically relevant oxides such as zirconium. (3) We have developed a photocatalytic strategy for the synthesis of colloidal Ag-TiO₂ nanorod composites, in which each TiO₂ nanorod contains a single Ag nanoparticle on its surface. (4) We have studied the contribution of the hollow geometry to the enhancement in photocatalysis. (5) We have also explored the use of photocatalyst for designing a novel photoreversible color switching system. Regarding the photophysical and photocatalytic characterization of the catalysts, we continue to

use both time-resolved photoluminescence and diffuse reflectance femtosecond transient absorption spectrometer to probe charge transfer dynamics in organic charge transfer crystals and nanostructured oxide compounds. Those studies are correlated with photocatalytic activity measurements in terms of hydrogen production from aqueous solutions. Last year we identified clear correlations among the lifetime of the fluorescence decay, the rate at which hydrogen is produced in photocatalysis, and the crystallinity of the titania shells using well-defined Au@Void@TiO₂ yolk-shell nanostructures. Our photophysics results suggests an alternative pathway to that commonly reported for the role of the metal that does not involve electron transfer to the metal but requires it to act as a catalyst for the recombination of the hydrogen atoms made via the reduction of protons on the surface of the semiconductor instead.

DOE National Laboratories

Metal and Metal Oxide-Supported Platinum Monolayer Electrocatalysts for Oxygen Reduction

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Funding: \$699,000 (2014)

PROGRAM SCOPE

This project contributes to resolving major problems in electrocatalysis important in chemical-to-electrical energy conversion in fuel cells, or electrical-to-chemical energy conversion in water electrolysis or carbon dioxide (CO₂) reduction. It focuses on the study and control of the electronic, structural and reactivity properties of promising nanostructured electrocatalysts. Great success has been achieved using platinum monolayer electrocatalysts, whose monolayer shell properties can be tuned by interactions with an underlying core to improve activity and durability for difficult reactions such as oxygen reduction or alcohol electro-oxidation, while reducing noble metal content to reduce cost. Efforts in 2014 continue to address the long-lasting challenge of shifting oxygen reduction reaction potentials close to thermodynamic reversible values. Such efforts include use of fluorinated chain molecules to decrease H₂O activity on Pt and increase near-surface O₂ concentration to enhance splitting the O-O bond (“dry cave” effect). We are also examining onion-structured nanoparticles with cores of multiple metal layers to facilitate reaching this goal, supported by DFT calculations. A broad study of enhanced kinetics and reaction mechanisms of the oxidation of alcohols (methanol, ethanol) on Pt monolayers under tensile strain is underway. Studies of ordering at the core-shell interface to increase stability and activity of electrocatalysts will be continued, as well as the design of a micro-reactor for electron microscopy studies of catalysts. Nitriding of non-noble components of core-shell catalysts will be explored to increase their catalytic activity and stability. By kinetic modeling and computational methods, we will obtain deeper insight into the kinetics and mechanisms of the O₂ reduction reaction, and alcohol oxidation.

FY 2014 HIGHLIGHTS

A distinct class of oxygen reduction (ORR) core-shell electrocatalysts comprised of nitride metal cores enclosed by thin Pt shells has been synthesized. Our theoretical analysis and the experimental data indicate that metal nitride nanoparticle cores significantly enhance the ORR activity in the order of PtNiN/C > PtFeN/C > PtCoN/C as a consequence of combined geometrical, electronic and segregation effects on the Pt shells. DFT calculations have shown a volcano type behavior with PtNiN/C at the top of the curve revealing the fact that, among the catalysts investigated, it has the best combination of both the surface strain and d-band center shifts. A structurally ordered Au₁₀Pd₄₀Co₅₀ catalyst exhibits comparable activity to Pt/C in both acid and alkaline media. Electron microscopic techniques demonstrate that via addition of Au atoms PdCo nanoparticles undergo an atomic structural transition from core-shell to a rare intermetallic ordered structure with twin boundaries forming stable {111}, {110} and {100} facets. The stability superior to Pt/C in alkaline media is attributed to the atomic structural order of PdCo nanoparticles along with protective clusters of Au atoms on the surface. This new strategy of making ordered Pd intermetallic alloy nanoparticles can be used in varied heterogeneous catalysis where size and structural stability matters. The splitting of the C-C bond in ethanol oxidation was observed on Pt monolayer under tensile strain on Au nanoparticles, while that was not observed with extended surfaces. Further work is needed to explain this difference. We demonstrated the effect of oxide co-catalysts on Pt/Au surfaces that helps oxidation and removal of CO that enhances the ethanol oxidation rate.

EARLY CAREER: Adsorbate Interactions in Catalytic Trend Studies

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Funding: \$500,000 (2014)

PROGRAM SCOPE

There is a constant drive toward more energy- and resource-efficient technologies, for example related to the use of natural gas or biomass, and new sustainable energy processes. A key element in most novel energy technologies is the need for new, efficient catalysts made from Earth-abundant materials. The atomic-scale design of catalytic materials with tailored properties thus represents a grand challenge for science and technology. Computational catalyst search approaches leveraging electronic structure theory-based atomic-scale simulations coupled with kinetic models provides a promising avenue for accelerating catalyst discovery efforts. To reliably address detailed catalytic properties, such as for example product selectivity, the currently available simulation accuracy needs to be significantly improved. The absence of suitable models for reliably including interactions between adsorbates on a catalyst surface presents a leading contribution to the inaccuracy in computational catalysis trend studies. This project aims to improve the fundamental understanding of the interactions between adsorbed atoms and molecular fragments on transition metal surfaces and devise models to include these interactions in catalytic trend studies. The scientific insights and the set of tools established in this project aim to create a break-through in obtaining quantitative agreement between theoretical catalysis studies and experimental measurements and could potentially become a cornerstone in establishing an accurate and reliable "Catalyst Genome". The tools will be applied to catalytic processes pertaining to the transformations and eventually the liquefaction (Fischer-Tropsch) of methane. This could ultimately lead to improved processes for utilization of natural gas resources.

FY 2014 HIGHLIGHTS

In earlier work a model for differential adsorption energies was established and used to analyze catalytic trends in the methanation and the steam reforming reactions. In FY14 we have developed a more complete model for integral adsorption energies in the presence of adsorbate-adsorbate interactions. This model can then be differentiated to obtain appropriate models of differential adsorption energies to be used in microkinetic trend studies. Whereas the accurate description of differential adsorption energies is the key ingredient in microkinetic models, the integral adsorption energy is essential for accurately describing for example adsorption-corrections to surface free energies. This makes the integral adsorption energy model a key ingredient in the accurate modeling of the morphology of transition metal catalyst nanoparticles in reactive environments. Another highlight has been the extension of the model for adsorbate-adsorbate interactions to multi-site surface facets of higher complexity than the close-packed fcc(111) facet. As many (if not most) interesting catalytic reactions take place on steps, defects or other under-coordinated surface sites, we have worked on devising a model, which adequately describes the interactions between ensembles of different sites on transition metal surfaces. The combined integral-multisite adsorption model has been used to re-analyze trends for methanation, synthetic natural gas synthesis, steam reforming, and for dry reforming of methane. This strengthens the foundations under the future analysis of the more complex selectivity issues present in the Fischer-Tropsch synthesis reaction.

Catalysis Science Program

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Funding: \$2,098,000 (2014)

PROGRAM SCOPE

The unifying theme in our research is the investigation of catalytically active metal centers whose nuclearity is limited to single metal atoms. The molecular uniformity of metal complexes studied in the field of homogeneous catalysis has been a major factor for the success of the field in the elucidation of reaction mechanisms and the understanding of catalytically active sites. We demonstrated previously the ability to synthesize isolated, ionic metal sites immobilized on hard supports such as SiO₂ and designer porous organic polymers (POPs) containing catechol and binol groups. Through the study of these catalysts we have shown that highly stable single-atom sites can be prepared and are catalytic for a variety of C-H activation and other catalytic transformations. For example, robust single-atom sites are highly selective and stable for alkane dehydrogenation at high temperature, but with low rates. By changing the ligand environment of the same transition metal, we have recently demonstrated much higher rates at lower temperatures while retaining high selectivity. We are interested to understand the factors which lead to higher activity by changes in the coordination environment around the metal, for example, the support type, redox active surface bonds, and changes in the metal-ligand bond strength tuning. In order to demonstrate enhanced rates and compare catalysts with differing thermal stability, we are determining the kinetics for alkane activation via dehydrogenation at high temperature and olefin-alkane hydrogen transfer at low temperature. State of the art *in situ* and *operando*

characterization using infrared, Raman and X-ray absorption spectroscopy, will provide information on the local structure of the site (number and type of metal-ligand and metal-support bonds, their distances, etc.), the oxidation state, and the intermediates formed under reaction conditions.

FY 2014 HIGHLIGHTS

Five different 1st row transition metal precursors (V^{III}, Cr^{III}, Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}) were successfully incorporated into a catechol POP (catPOP A₂B₁) support and characterized using ATR-IR and XAS analysis. The resulting metallated POPs were then evaluated for catalytic alkyne hydrogenation using high-throughput screening techniques. All six POPs were unexpectedly found to be active and selective catalysts for alkyne semi-hydrogenation. Three of the POPs (V, Cr, Mn) are the first of their kind to be active single-site hydrogenation catalysts. These results highlight the advantages of using a POP platform to develop new catalysts that are otherwise difficult to achieve through traditional heterogeneous and homogeneous routes. *Angewandte Chemie International Edition* 2014, 126, 12251-12254

Strategic Design of Novel Catalysts for the Selective Synthesis of Fuels and Chemicals

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Funding: \$1,969,000 (2014)

PROGRAM SCOPE

The present program is focused on the strategic design of novel catalysts of potential interest for the production of fuels and chemicals in an energy-efficient and environmentally acceptable fashion. Of particular interest are the conversion of alkanes to alkenes and functionalized products, and the synthesis of fuels and chemicals from carbon monoxide and carbon dioxide. To achieve these goals a molecular understanding of catalytically active centers is used together with knowledge of how to synthesize unusual chemical and physical environments at such centers. The program involves a synergistic combination of efforts in the areas of catalyst synthesis, characterization, and evaluation. Quantum chemical simulations of catalytically active centers help guide the interpretation of experimental findings and suggest novel structures to be attempted synthetically. The seven principal investigators - Alexis T. Bell (ATB), Robert G. Bergman (RGB), Christopher Chang (CC) Enrique Iglesia (EI), Kenneth N. Raymond (KNR), Gabor Somorjai (GAS), and T. Don Tilley (TDT) pursue independent research goals while extensively collaborating via joint supervision of graduate students and postdoctoral associates, and by extensively sharing instrumentation.

FY 2014 HIGHLIGHTS

Showed that dianionic square planar cobalt(II) complex activates dioxygen to produce reactive intermediate that cleanly cleaves range of C-H bonds likely through cobalt(IV) oxo. Prepared dantalum center supported by silsesquioxane ligand that models selective silica-supported epoxidation catalysts and provides correspondingly selective homogeneous epoxidation catalysts. Devised strategy to control electron density at metal center via remote chemical trigger involving second-sphere Lewis acid binding. New examples of appropriate ligand-Lewis acid pairs developed for triggering reductive elimination and C-H activations at Pt center. Showed that self-assembled supramolecular host catalyzes Nazarov cyclization with rates over a million times faster than that of background reaction. Showed that supramolecular host catalyzes substitutions at secondary benzylic carbon with retention of configuration as opposed to inversion of configuration in bulk solution. Such control of stereochemistry is unprecedented with supramolecular host-guest catalysis. Generated water-soluble iron-oxo complexes supported by polypyridine ligands; evaluated their reactivity for C-H oxidations. Prepared and characterized series of new iron-based catalysts for CO₂ and proton reduction. Developed hybrid cell-nanoparticle system for electrochemical CO₂ reduction. Developed genetic selection for increasing fuel titers in engineered bacteria. Isolated and sequenced strains with improved fuel production efficiency under production conditions. Showed that proximity between Pt metal clusters and Brønsted acid sites at nanometer scale within confined environments leads to much higher turnover rates for bifunctional cascades leading to hydrodeoxygenation of butanols and alkyl phenols than on solids of similar composition but with intersite distances in micron scale. Identified evidence for strain effects on activity of isolated tungstate species supported on silica used for metathesis of propene.

Studies on Homogeneous Catalysis for Efficient Synthesis from Chemical Feedstocks

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Funding: \$485,000 (2014)

PROGRAM SCOPE

This FWP strives to establish the foundation upon which to design new catalysts and catalytic processes for chemical synthesis. The research has encompassed reactions catalyzed by transition metal catalysts that form both carbon-carbon and carbon-heteroatom bonds in products that have typically required multi-step syntheses from common chemical feedstocks. This program addresses several goals of the Basic Energy Sciences mission. It will create fundamental understandings that elucidate catalyst structure-reactivity relationships needed to design future systems, will use this information to develop new catalytic reactions that make more efficient use of energy resources and carbon feedstocks, and will address the need to develop chemical reactions that have reduced environmental impact. The current application includes proposed work to continue fruitful studies on additions of amines and alcohols to alkenes, as well as to investigate new topics related to the additions of C-H and X-H bonds to alkenes and new approaches to the discovery of catalytic reactions. The proposed studies include Specific Aims to 1) identify amido and alkoxo complexes that insert alkenes under mild conditions and to understand the factors that control the rates of these reactions; 2) develop iridium and enzymatic systems that catalyze the additions of N-H and O-H bonds to unactivated alkenes; 3) develop new

catalysts for the addition of aromatic C-H bonds to alkenes; and 4) expand the scope of our studies on high-throughput evaluation of catalyst activity to identify new transformations catalyzed by complexes of underutilized classes of ligands and first-row metals.

FY 2014 HIGHLIGHTS

Completed initial studies and reported the first hydroarylations of unactivated alkenes occurring with high anti-Markovnikov regioselectivity. Discovered and reported the oxidative olefination of furans with unactivated alkenes. Discovered the first intermolecular addition of indole N-H bonds to unactivated alkenes. Characterized the first single-site artificial organometallic protein and observed the first reaction of an organometallic protein to both cleave and form a metal-carbon bond. Developed an automated algorithm to search for reaction products within a pool of reactants and catalyst components.

Multifunctional Catalysis to Synthesize and Utilize Energy Carriers

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Funding: \$7,157,000 (2014)

PROGRAM SCOPE

The central goal of this research program is to develop a fundamental understanding of catalytic processes for hydrogen management in the conversion of biogenic resources and CO₂ directly to energy

carriers, to use this knowledge to synthesize new catalysts, and to design new catalytic routes to energy carriers. We surmise the need for multi-functional catalytic sites, as well as for sterically assembling various sites to enable cascade strategies for effecting complex transformations. Throughout the organization of this program we integrate heterogeneous and homogeneous catalysis, surface science and computational methods. The research will focus on the grand challenges described in this quote from the U.S. Department of Energy (DOE) Basic Energy Sciences (BES)-sponsored report Basic Research Needs: Catalysis for Energy: "To realize the full potential of catalysis for energy applications, scientists must develop a profound understanding of catalytic transformations so that they can design and build effective catalysts with atom-by-atom precision and convert reactants to products with molecular precision."

FY 2014 HIGHLIGHTS

- Catalysts, containing both acid and metal active sites, for lignin conversion were investigated in reactions involving model substrates such as phenolic ethers, phenols, alcohols and olefins. Individual steps of these reactions were studied to understand the guiding principles for further catalyst design at both atomic and mesoscale level.
- An unexpected bimolecular dehydrogenation reaction pathway for diols on TiO₂(110) was uncovered. H₂ formation from this unusual reaction arises from hydroxyl groups of adjacently-adsorbed diols and, as such, is highly sensitive to the steric environment around these ⁻OH groups.
- Using fundamental thermodynamic data, a catalyst for CO₂ hydrogenation was designed based on molecular cobalt complexes. This new catalyst has a higher catalytic performance than the fastest precious metal analogs. We are now extending this concept to aqueous catalysis for CO₂ hydrogenation.
- Carbonates were established as major intermediates in heterogeneous phase catalytic hydrogenation of CO₂ on multifunctional metal/metal-oxide catalysts. Further, a low temperature/pressure CO₂ conversion via alkylcarbonate intermediates was demonstrated in a carbon capture solvent.
- Mechanistic studies of water and simple probe molecules were completed on TiO₂(110) and RuO₂(110) using a variety of experimental and theoretical approaches. We focused on the roles of defects, coadsorption, site specificity and reaction dynamics on single electron transfer photochemical events.
- Capabilities and expertise were developed to provide the first experimental measure of reaction rates, turnover frequencies and thermodynamic driving force for the catalytic hydrogenation of imines, olefins, aldehydes and ketones. We have carried out the first quantitative measurements of the reactivity of frustrated Lewis pairs, as nonmetallic hydrogenation catalysts.

Predictive Theory of Transition Metal Oxide Catalysts

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Funding: \$970,000 (2014)

PROGRAM SCOPE

The work focusses on establishing a predictive theory for transition metal oxide catalysis. It addresses the fundamental challenges associated with the electronic structure description of transition metal oxide surfaces, such as the electron localization in oxides and its effect on adsorption properties. The goal is to combine experimental and theoretical methods to establish an accurate theory for transition metal oxide surfaces, which potentially could create the foundation for tailoring new oxide catalysts.

FY 2014 HIGHLIGHTS

As a first step towards a database of adsorption and activation energies for oxide surfaces, we performed a theoretical investigation of surface properties and energetics of molecules and oxygen chemistry on low-Miller index surfaces of alkaline-earth metal oxides (MgO, CaO, SrO, BaO). The accuracy of commonly used xc functionals and RPA was evaluated and compared to experiments. All considered functionals qualitatively predict similar adsorption energy trends and the calculated and experimental adsorption energies lie within the bounds of LDA (too high) and RPBE (too low). The ordering between adsorption energies on different surface facets is attributed to the local geometrical and electronic surface structure of the metal constituent of the oxide. We have worked to extend the *ab initio* nanoreactor to problems involving heterogeneous catalysis with the first target to explore the Fischer-Tropsch reaction on iron and iron/silica for direct nonoxidative conversion of methane to ethylene, aromatics and hydrogen (Nature Chem. 6, 1044 (2014)). The basic idea of the nanoreactor is to use *ab initio* molecular dynamics to sample the space of chemical reactions, which are monitored by pattern recognition algorithms. We added effective core potentials (ECPs) to describe the metal atoms to our GPU-based code, which required development of a GPU-based algorithm for the ECP integrals. We also incorporated fractional occupation in the self-consistent field procedure to be able to sample several spin states, necessary when modeling metal clusters. Finally, we incorporated new boundary conditions for a surface nanoreactor – augmenting the spherical nanoreactor with a disc-shaped region representing the surface not subject to periodic confining potential. A key element in testing new computational approaches for oxide surface chemistry is to compare their results to accurate experimental adsorption energies for well-defined systems.

SUNCAT Center for Interface Science and Catalysis

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Funding: \$2,425,000 (2014)

PROGRAM SCOPE

The SUNCAT Center for Interface Science and Catalysis seeks to develop a fundamental understanding of the electronic and structural factors determining the catalytic properties of solid surfaces. The ultimate aim and test of success is to provide design tools for new catalysts. We propose to further develop the SUNCAT-FWP to include new levels of complexity: more complex molecules and processes, more

complex multi-functional active sites and support effects, more complex bonding types, and more complex electronic structure methods. Our strategy will be to develop concepts that reduce the complexity to manageable descriptor-based models and enable an understanding of trends from one catalyst system to the next. The concepts are tested on a number of processes for energy transformations: Higher alcohol synthesis from syngas, direct conversion of methane to methanol, and metal-air batteries.

FY 2014 HIGHLIGHTS

Highlight from 2014 include the development of a first method to include uncertainty in the calculation of complex properties like catalytic reaction rates (Science 445, 197), new insights into limitation in electrochemical performance due to charge transport in insulating catalysts (Nano Lett. 14, 5853), new ideas for ammonia synthesis catalysis at low temperature and pressure (Chem Phys. Lett. 598, 108), discovery of a new class of catalysts for CO₂ reduction to methanol (Nature Chem. 6, 320), new insight into electronic structure effects in surface reactivity of transition metals (Phys. Rev. B 89, 115114), the first analysis of trends in selectivity and activity of catalysts for higher alcohol synthesis from CO and H₂ (Top. Catal. 57, 135), theoretical predictions and direct experimental observation of intermediates in the electrochemical oxygen reduction reaction (Nature Comm. 4, 2817), and new catalysts for the oxygen reduction reaction (ChemElectroChem 1, 67).

Fundamentals of Catalysis and Chemical Transformations

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Funding: \$2,289,000 (2014)

PROGRAM SCOPE

The overarching goal of this proposal is to understand molecular interactions and reactions at the surfaces of catalytically active oxides and functionalized oxides. There is particular emphasis on oxygenated molecules and their thermal chemistry, surface chemistry and catalytic conversion which links all tasks of the proposal. Catalytic systems of interest include cerium oxide as a model crystalline, reducible oxide, other oxides with controlled morphologies, and Au in various forms including nanoparticles, well defined clusters (Au_n(SR)_m) and single sites. Model oriented thin films of CeO₂ with (100) and (111) surface terminations are compared to uniformly structured CeO₂ nanoshapes (cubes, octahedra) which manifest these surface terminations. These surfaces and nanoshapes are used to explore the effect of site geometry on catalytic behavior as a basis for learning how to tailor catalytic selectivity via structural differentiation. Selectivity and rates of catalytic reactions of C₁ and C₂ alcohols,

aldehydes and acids are compared to learn how surface sites geometry and cooperativity between cation and anion sites affect reaction pathways. Surface reactions on oriented films are probed in UHV by synchrotron based electron spectroscopies. Nanoshapes are used directly in flow reactors to probe catalytic behavior and explore reaction pathways using operando Raman and IR spectroscopies and a variety of temperature programmed and catalytic measurements. Reactions are modeled computationally using DFT. Studies are underway to explore the how functionalization with acidic or basic sites affects surface adsorption and catalytic properties. The effects of the stabilizing ligands upon stability of Au clusters and the structural changes that occur upon ligand removal are being studied. The proposed research is aligned with the grand challenges described in the BES Basic Research Needs Workshop Report on Catalysis for Energy.

FY 2014 HIGHLIGHTS

We have pursued three focus areas. First, catalytic reactions of small oxygenates on model CeO₂ surfaces were explored to obtain a fundamental understanding of reaction pathways and the relationship between surface structure and catalytic function. It was shown that CO₂ adsorbs on a CeO₂(100) in a flat-lying tridentate configuration. This novel bonding is unexpected since carbonates are usually thought to form mono- or bi-dentate adsorption configurations. Reaction of acetaldehyde over CeO₂ nanoshapes produce crotonaldehyde and various other products. Selectivity can be attributed to the variation in the basicity of the surfaces, defects densities, coordination numbers of surface atoms, and reducibility. DFT calculations clarified the origin of the selectivity differences between the CeO₂(100) and (111) surfaces for the ethanol selective oxidation. Transition states computed for α - and β -CH bond cleavage explained the experimentally measured selectivity. In the second focus area, we have explored supported molecular Au clusters of well-defined sizes. We have studied the stability and reactivity of Au cluster compounds on uniformly structured CeO₂ supports as a route to structurally defined metal catalysts. Ligands play a key role in stabilizing the Au clusters, but are found to poison the activity of the Au catalytic sites. Cationic Au sites are found to play a major role in CO oxidation, which proceeds predominantly via a redox mechanism where CeO₂ activates O₂ while CO is activated on the de-thiolated gold sites. In the third focus area, we have explored synthetic routes to achieve selectivity in catalysis. A lab-in-a-shell strategy was developed for the preparation of multifunctional core-shell nanospheres consisting of a core of metal clusters and an outer microporous silica shell. Pd clusters encapsulated in hybrid core-shell structures exhibit size-selective catalysis in allylic oxidations of substrates with the same reactive site but different molecular size.

Homogeneous and Interfacial Catalysis in 3-D Controlled Environments

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Students:	2 Postdoctoral Fellow(s), 12 Graduate(s), 0 Undergraduate(s)
Funding:	\$1,254,000 (2014)

PROGRAM SCOPE

This program brings together the best features of homogeneous and heterogeneous catalysis by designing novel single-site mesoporous interfacial catalysts with controlled, nanostructured morphology and surface properties. The control of specific chemical properties, spatial distribution, and concentrations of various catalytic functional groups on the pore walls is achieved by a synthetic approach referred to as multifunctionalization, where some of the anchored groups serve as a catalyst, while others are designed to modify the selectivity or activity of the system. We seek to advance the physico-chemical characteristics of mesoporous scaffolds, understand and address the effects of transport and confinement on catalytic transformations, and develop improved organometallic ligands for energy-related catalytic transformations. These new single-site heterogeneous catalysts are amenable to precise characterization by a combination of chemical, physical and computational methods. Solid-state NMR methodology is developed and applied as the primary analytical tool for studying their structure and functioning. The catalytic activity is being examined in several distinct classes of chemical reactions, including enantioselective hydrogenation, hydrolysis, polymerization and oxidation. Detailed mechanistic studies are carried out in an effort to recognize the key factors that determine selectivity, reactivity and kinetics in both homogeneous and heterogeneous catalytic chemistry. Our team gains fundamental knowledge about the influence of the 3-D environment on catalysis. In the long term, such fundamental knowledge will create a basis for the design of efficient, stable, and highly selective catalytic systems that for specific applications in the production of fuels and chemicals.

FY 2014 HIGHLIGHTS

We developed, characterized and tested a new silica-supported zirconium catalyst for the hydroboration of aldehydes and ketones. This novel material remained catalytically active upon recycling or exposure to air, showing that these single-site zirconium centers are robust catalytic sites for carbonyl reduction. Most importantly, this system highlights the possibility of using abundant oxophilic early metal catalysts for the conversion of highly oxidized substrates relevant to new chemical feedstocks. The mechanistic details of carbon-carbon coupling reactions catalyzed by amine-modified mesoporous silica nanoparticles were investigated using theoretical models, kinetic measurements and solid-state NMR spectroscopy. These studies led to the assembly of multicatalytic systems that performed tandem reactions for upgrading the molecular weight of alcohols. The general strategy consisted in the assembly of two site-isolated catalysts: the first enabling low temperature oxidation of alcohols to aldehydes, and the second facilitating aldol condensation between the intermediate aldehydes. Site-isolation was achieved by immobilizing one catalyst inside of the pores, while the other catalyst was bound to the external surface of the particles. This isolation prevented mutual poisoning of the catalysts. The versatility of this method of assembly was proven by combining an organocatalyst with a second organocatalyst, an enzyme, or a metal nanoparticle.

Catalysis Science for Advanced Fuels

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Funding: \$1,645,000 (2014)

PROGRAM SCOPE

This program pursues an improved understanding of chemical catalysis for advanced fuels synthesis and energy conversion processes by elucidating catalytically important properties of well-defined surfaces, powders and nanostructures. Complexities stemming from the inherent multi-component aspects of heterogeneous catalysis are explored using both ultra-high-vacuum surface science investigations of well-defined model systems, and powder diffraction and x-ray absorption studies of 'real-world' systems. Two subtasks bring distinct methods to common reaction themes in fuel synthesis such as desulfurization, hydrogen production and oxygenate synthesis. The subtask Catalysis: Reactivity and Structure develops and applies new approaches for the in-situ characterization of heterogeneous catalysts using facilities available at the National Synchrotron Light Source for X-ray diffraction, X-ray absorption and photoemission. Quantum-chemical computation plays an essential role for basic understanding of catalytic reactions and interpretation of experimental results. The subtask Nanostructured Materials for Catalysis focuses on the preparation, characterization and reactivity of metal nanostructures. Its goals are to identify and characterize the catalytically active sites of supported nanocatalysts and to investigate the influence of particle size, morphology and support on nanostructure reactivity. Nanostructure synthesis and characterization benefit from collaboration at the Center for Functional Nanomaterials. Nanocluster preparation techniques include soft-landing of size-selected clusters and reactive layer deposition.

FY 2014 HIGHLIGHTS

The research themes in this FWP are inspired by challenges in the production and use of chemical fuels. In the last year important contributions have been made in areas related to (1) the cleaning of oil-derived fuels through hydrodesulfurization, (2) the reforming of alcohols, (3) the synthesis of higher (C_1 - C_4) alcohols by the hydrogenation of CO_2 or CO, and (4) CO oxidation. The last two topics are associated with C_1 chemistry. These research efforts were also linked by an interest in the properties of oxides, carbides and sulfides, materials which may be able to replace scarce noble metals in energy-related catalysis. In many of our studies, the catalytic processes took place on multifunctional catalysts which contained metal-oxide, metal-carbide or metal-sulfide interfaces developed in the subtask on Nanostructured Materials. A paper was published in Science describing a novel and highly active catalysts, $Cu/CeO_x/TiO_2$, for the hydrogenation of CO_2 to methanol. In addition, it was shown that Au deposited on carbide supports such as TiC and MoC is an excellent catalyst for desulfurization reactions, the oxidation of CO and the transformation of CO_2 to methanol. Studies were performed examining the properties of a highly efficient non-expensive Ni-CeO₂ catalyst active for the production of hydrogen through the reforming of ethanol. The development of techniques for characterizing the structural properties of catalysts under the high-pressure conditions of industrial processes is a top priority for this project. In the last year, the Catalysis Group at BNL has been very active in developing instrumentation for the characterization of catalysts with PDF analysis and the integration of XAFS and XRD or XAFS and IR or Raman. The integration of IR and Raman with XAFS allows a simultaneous determination of the reaction intermediates on the surface and the chemical state and structure of the catalyst.

Mechanisms for Water Gas Shift Reaction

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Funding: \$631,000 (2014)

PROGRAM SCOPE

The water-gas shift reaction (WGS: $\text{CO} + \text{H}_2\text{O} = \text{H}_2 + \text{CO}_2$) is a critical process in providing pure hydrogen for fuel cells and other applications. Improved air-tolerant, cost-effective WGS catalysts for lower temperature processing are needed. Ceria-, titania- and molybdena-based catalysts are expected to be the next generation of WGS catalysts for industrial applications. The design and optimization of these WGS catalysts depends on a better understanding of their structures and functions. This project involves a coordinated research program to understand the active sites and reaction mechanism for the WGS on these promising metal/oxide catalysts. Our goal is to develop the ability to predict, and ultimately design, improved cost-effective WGS low temperature catalysts. Our approach exploits a uniquely powerful combination of synthetic and characterization methods for both model systems and industrially relevant powder catalysts. It utilizes unique capabilities for in-situ studies using time-resolved X-ray diffraction, X-ray absorption spectroscopy, photoemission, infrared spectroscopy and transmission electron microscopy. Most experiments are closely coupled to theoretical studies on the chemisorption of the reactants, the stability of possible intermediates, and activation barriers for elementary reaction steps, providing critical guidance in developing a complete picture of the links between catalyst structure and reaction mechanism in this important process for the production of pure hydrogen.

FY 2014 HIGHLIGHTS

More than ten papers in topics related to the water-gas shift reaction were published. There were important advances in six general areas.

- 1) Systematic studies using a suite of in-situ techniques (XRD, PDF, XAFS, AP-XPS, IR) showed that the structure and composition of metal/oxide catalysts used for the water-gas shift are dynamic entities that change with the system temperature and the pressure of the reactants.
- 2) New type of metal-support interactions were discovered while examining the behavior and properties of metal/oxide and metal/carbide catalysts. These metal-support interactions can be quite useful for the rational design of low-temperature water-gas shift catalysts.
- 3) It was shown that the metal and support phases of metal/oxide and metal/carbide catalysts must be taking into consideration when designing highly-efficient catalysts for the water-gas shift.
- 4) Theoretical studies showed that a HOCO species, formed at metal-oxide and metal-carbide interphases, is a key intermediate during the water-gas shift.
- 5) Highly active powder catalysts that combine Au or Pt on $\text{CeO}_x/\text{TiO}_2$ and MoC_x substrate were prepared and fully characterized.
- 6) The scientists in the project participated in the development of new tools or techniques for the in-situ characterization of water-gas shift catalysts, helping in the design of a new instrument that will combine PDF or XAFS with infrared or Raman spectroscopy. This new instrumentation will allow us to perform unique mechanistic studies.

EARLY CAREER: Catalyst Biomimics: A Novel Approach in Catalyst Design

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Funding: \$2,500,000 (2010-2014)

PROGRAM SCOPE

The objective of the proposed research is to incorporate a rationally designed proton channel into homogeneous catalysts using advanced enzyme design methodology combined with superior molecular catalyst design. Proton channels are essential for the rapid rates of hydrogen production/oxidation observed in enzymes and small molecule catalysts are notably unable to match these rates. We propose to design synthetic catalysts with an enzyme-like proton channel while maintaining a relatively small catalyst. Using Rosetta, energy minimized computational structural models will be generated to develop peptide ligands with positioned proton relays. The computationally determined “best” ligands will be synthesized and incorporated into nickel based catalysts. The catalyst will be characterized using electrochemistry, NMR, IR, XAFS and X-ray crystallography. Attributes such as the pK_a , distance, structural flexibility and number of the relays will be probed. The multistate empirical valence bond approach will be used to predict which stabilized structures might perform better than others based on pK_a values and preferred proton transport pathways. This molecular level approach will allow us to develop a detailed understanding of proton relays, revealing insights into how they can enhance homogeneous catalysts, as well as how they function in enzyme systems, with potential applications to energy and fuel storage.

FY 2014 HIGHLIGHTS

In the past year, we have achieved several key accomplishments. We successfully incorporated a structured peptide into a hydrogen production catalyst and demonstrated its function. While the resulting complex was twice as fast as the parent catalyst with no peptide, the most important result is that this complex can serve as a foundation upon which to develop a more complex outer coordination sphere, whose features can be tested to provide a mechanistic understanding of its role. We also reported on development of the first water soluble hydrogen oxidation catalyst, where solubility was enabled by an attached amino acid (glycine), which also served to create a two-relay proton channel. Modifying glycine to an arginine resulted in the fastest H_2 oxidation catalyst reported to date at room temperature, and exceeding the rates of enzymes by several orders of magnitude at elevated pressures of H_2 . This remarkable performance is thought to be due to the arginines controlling the active site structure. This complex was further found to be truly reversible while maintaining fast rates in both directions, something only ever observed before in enzymes and representative of achieving the highest efficiency attainable. The reversible behavior was found to be due to a combination of the outer coordination sphere, the solvent and the thermodynamic matching of the 1st and 2nd coordination spheres.

Nanoscience and Nanoparticles for 100% Selective Catalytic Reactions

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Funding: \$776,000 (2014)

PROGRAM SCOPE

Heterogeneous catalysts are nanoparticles. They are utilized in most industrial chemical processes in the form of metal clusters dispersed on high surface area oxide supports. Recent breakthroughs in nanotechnology have created the ability to control material structures on scales that are relevant for catalyst design (e.g., the diffusion length of molecular intermediates in a bifunctional catalyst, ca. 5 nm). The goal of this project is to explore the molecular and nanoscale variables, structure, composition and dynamic properties of catalysts to achieve 100% selectivity in multipath surface catalyzed reactions. The three main areas of emphasis that are combined in this program: to fabricate 3-dimensional or 2-dimensional catalyst systems with complete control of catalyst nanoparticle location, structure, thermal and chemical stability; to characterize these nanoscale systems by a combination of steady-state and time-resolved and spectroscopic techniques that identifies their size, location, electronic structure and composition during and after fabrication and under reaction conditions; to carry out multipath chemical reactions and correlate reaction selectivity with the physical-chemical variables of nanoparticle catalyst fabrication with in-situ probes of the catalyst surface, if possible.

FY 2014 HIGHLIGHTS

Studied hydrogenative isomerization of hexane and methylcyclopentane over Pt nanoparticles (2.5nm) supported in mesoporous oxides (e.g. V, Nb, Sn and Al modified silica) and zeolites of BEA and ZSM-5 framework structures. Conducted hydrogenation of CO and CO₂ to produce hydrocarbon fuels using size-controlled Co nanoparticles (3-10nm) supported in mesoporous metal oxides such as TiO₂, Co₃O₄ and MnO₂. Oxidative conversion of simple alcohols (methanol, ethanol and propanol) was studied in both liquid-solid and gas-solid interfaces over size-controlled Pt nanoparticles in the 1-5nm range. Detected a transient intermediate of gold-catalyzed arylative ring expansion under reaction conditions in solution by rapid-scan FT-IR spectroscopy; elucidated kinetic behavior. Determined structure of this intermediate based on identification of 6 vibrational modes revealing chemical bond rearrangements during rate limiting step. (Specifically, the intermediate features an expanded ring and the step involves transfer of aryl group from Au center to the alkyl side chain under expulsion of Au moiety to form final product under regeneration of free catalyst). Determined the efficiency, lifetimes and mechanisms of several light driven Ru and Ir redox sensitizers by combined transient FT-IR and optical spectroscopy for pulsed activation of catalysis in solution through redox activation of catalyst (soluble Au catalysts and supported Au clusters are first application). Spectral mapping of a multistep gold-catalyzed rearrangement in a flow microreactor performed with a spatial resolution of 15 micrometers, employing micrometer-sized synchrotron-based IR and X-ray beams. *In situ* synchrotron-sourced IR microspectroscopy detected conversion of reactant into primary product which was catalytically transformed into secondary product. By tuning residence time of reactants in flow microreactor, performed detailed an analysis of reaction kinetics.

Computational and Theoretical Chemistry

Institutions Receiving Grants

Understanding Electron Transfer in Plasmon-Enhanced Photocatalysis using Nonadiabatic Electron Dynamics

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Funding: \$359,950 (2014-2016)

PROGRAM SCOPE

Plasmon-enhanced photocatalysis is a promising method for the generation of solar fuels. In plasmon-enhanced photocatalysis, noble metal nanoparticles (NPs) are interfaced with a semiconductor, and the combined system has increased photocatalytic yields when irradiated with visible light. However, there is currently a lack of understanding of the fundamental physical principles that underlie these systems. The goal of this work is to develop an essential understanding of the origin of plasmon-enhanced photocatalysis and the conditions that increase its enhancement. This investigation will involve studies of the electron and electron-nuclear dynamics in pure NPs as well as in systems that incorporate an interface between a metal NP and a metal oxide layer. To accomplish our goals, our investigation will begin at the first instance when solar photons interact with a metal nanoparticle and progress to systems that incorporate an interface between a large metal NP and a metal oxide layer. This requires a variety of theoretical techniques depending on the size and complexity of the system and the time scale of the processes involved. Initially, we will examine the electron dynamics in pure metal NPs using quantum mechanical methods including time-dependent Hartree-Fock and time-dependent density functional theory methods. In the next step of the research, we will examine how electron dynamics couple with nuclear dynamics to permit the excited electronic states generated by solar excitation to decay to lower energy states. In addition, we will examine how electrons transfer between a gold nanoparticle and a titanium oxide surface, which will likely depend on the linker between the NP and the surface, features of the surface such as defects, and the excitation wavelength. To treat some of the largest systems of interest in this work, we will develop and test a new nonadiabatic density functional tight binding approach.

FY 2014 HIGHLIGHTS

This project has just come online in the last couple months of FY 2014. Our group has installed the CPMD code and has begun examining how the memory requirements of TDDFT calculations increase with the size of the system. We have found that the memory requirements do not scale as N^3 or N^4 , where N is the number of basis functions in the system; we will continue to examine the memory requirements in order to learn more about the scaling. In addition, our group has begun to use the time-dependent Kohn-Sham approach to examine the electron dynamics of thiolate-stabilized nanoparticles including $\text{Au}_{18}(\text{SH})_{14}$, $\text{Au}_{25}(\text{SH})_{18} \dots \text{NH}^+$, and $\text{Au}_{38}(\text{SH})_{24}$. The Au_{18} system has recently been reported as a good sensitizer for photocatalysis, so we have added it to our original scope of work.

Theoretical Studies of Elementary Hydrocarbon Species and Their Reactions

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Funding: \$285,000 (2014-2015)

PROGRAM SCOPE

This research program carries out both methodological development and computational applications of *ab initio* quantum chemistry, as directed toward the fundamental chemical physics of combustion. To build and refine the world's database of thermochemistry, spectroscopy, and chemical kinetics, next-generation electronic structure methods are needed to achieve very high accuracy (0.1-0.2 kcal/mol) in theoretical predictions. Toward this ambitious goal, our work focuses on rigorous single- and multireference coupled cluster methods, executed to the level of triple or quadruple excitations and pushed to the complete basis set limit via new explicitly correlated techniques or more established extrapolation schemes. Another hallmark of this research is the treatment of molecular vibrational anharmonicity.

FY 2014 HIGHLIGHTS

Representative research topics recently pursued are as follows:

- (1) Radical-radical hydrogen abstractions in combustion chemistry are disproportionation reactions that are generally exothermic with little or no barrier, yet are underappreciated and poorly studied. These reactions usually begin with two free radicals and end with two closed-shell products, and thus the electronic transformation is intrinsically multireference in nature. Such challenging electronic structure problems have been tackled using our recently developed state-specific multireference coupled cluster methods Mk-MRCCSD and Mk-MRCCSD(T). The rigorous Mk-MRCCSD(T)/CBS results demonstrate unequivocally that the prototypical methyl + ethyl, H + ethyl, and H + HCO reactions are facile, proceeding with no barrier in the entrance channel.
- (2) The ubiquitous reactions of alkyl radicals with molecular oxygen rapidly become more complex as the radical grows in size. Isomerizations to hydroperoxyalkyl radicals (QOOH) are in competition with concerted elimination of HO₂. In a herculean investigation, all chemically relevant minima and transition states of the *n*-propyl, *i*-propyl, and *n*-butyl + O₂ systems are being mapped out using CCSD(T)/cc-pVTZ theory, and focal point analyses targeting the complete basis set limit of CCSDT(Q) are being executed to obtain definitive energetics.
- (3) The abundance of HOOO in combustion and atmospheric chemistry and the role of this poorly understood species as a sink for hydroxyl radicals has been a subject of recent debate. In a collaboration with the experimental group of Professor Gary Douberly, inertial dipole moment components were obtained from Stark spectra of the trans-HOOO radical in superfluid helium nanodroplets, and computations at the composite all-electron CCSDT(Q)/CBS level of theory were used to resolve the controversy over the structure of this species.

Towards 3rd Generation Organic Tandem Solar Cells with 20% Efficiency: Accelerated Discovery & Rational Design of Carbon-Based Photovoltaic Materials

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Funding: \$341,056 (2014)

PROGRAM SCOPE

The goal of this research effort is to expand the capabilities of the Harvard Clean Energy Project— our automated, high throughput screening framework for the virtual design and screening of potential organic photovoltaic materials – in order to accelerate development towards a material displaying 20% power conversion efficiency. In order to understand and characterize the electronic structure of these materials, CEP utilizes first principles quantum chemical calculations for multiple low energy geometries of each of the generated molecules – resulting in what we believe to be the world’s largest database of quantum chemical information. From the data that we collect, we aim to establish structure-property relationships which will aid the rational design of novel photovoltaic materials by identifying combinations of fragments which result in increased performance. These relationships will aid in the development of enriched libraries, allowing us to efficiently search chemical space, and focus computational resources on molecules which have high potential for displaying desirable properties. We augment this data-mining based approach with machine-learning techniques, which affords additional feedback, helping us to both improve the design of these molecules and predict the potential of newly generated molecules. This allows us to extend our search far beyond the scale which is feasible with an all-quantum-chemical approach. By distributing our calculations over thousands of volunteer computers using the World Community Grid, we can calculate properties for around 30,000 molecules a week. We estimate this resource to correspond to a 6-7,000 core computer cluster. The development of organic photovoltaic materials is one of the most exciting frontiers of renewable energy, and we believe that our high throughput approach has the potential to provide important contributions, as well as changing how science equips itself to answer such questions in the future.

FY 2014 HIGHLIGHTS

1. Expansion of the Harvard Clean Energy Project. Over 3 million compounds have now been screened, which has required over 300 million quantum-chemical calculations. This represents the largest known database of such information, and the data provided affords significant insight into factors determining the efficacy of molecules for use in OPVs. The project has thus far harvested over 29,000 CPU years from the World Community Grid.
2. Analysis of pairwise fragment frequencies from the CEP. A library of 2.1 million molecules was built from 26 fragments suggested by the Bao group and examined with quantum chemical calculations on the World Community Grid. High performing candidates have been extracted and used to aid in the design on new libraries. Pairs of fragments which were particularly effective, and those whose inclusion would result in poor device performance have been identified.
3. Generation of synthetically accessible libraries. One of the learning points from the initial round of investigation was of the importance of generating synthetically accessible libraries. This has

been achieved by investigating molecular reactivity, and by generating libraries of molecules with specific restraints. Molecular reactivity was investigated by data-mining the Reaxys database and correlating these results with calculated descriptors. Measures of accessibility have been calculated for libraries which have symmetry constraints placed upon the combinatorial growth, and these indicate improved synthetic accessibility.

4. Inclusion of machine learning techniques to the CEP. We have developed methods which combine molecular fingerprinting with neural networks and Gaussian processes to enable the fast screening and prioritization of molecules. Currently, Gaussian processes are able to predict the PCE to within $\pm 1\%$ - which is enough to vastly reduce the number of molecules screened. A multi-layer perceptron has been trained which can reduce this error.

Density Functional Based Tools for Simulation of Photo-Induced Charge Transfer

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Funding: \$390,000 (2014-2016)

PROGRAM SCOPE

The project concerns development and applications of efficient density functional theory based methods that can provide a framework to study the light-harvesting molecular systems. The goal is to gain the predictive capability of quantum mechanical computational methods, which could be used for high-throughput material screening. Such a framework needs to be efficient enough to handle large system sizes for molecular calculations since most of the interesting light-harvesting molecular systems contain hundreds of atoms. We have earlier demonstrated the predictive power of a density functional method for charge transfer excitations. It was shown that even using pure generalized gradient approximation to exchange-correlation functionals such systems could be described both efficiently and accurately. Further developments include calculation of other parameters such as electronic coupling from first principles which combined with the previous developments can be used to gain insight into photoinduced charge transfer process. Other related developments are based on incorporation of recent advanced density functionals, which are shown to better predict certain properties into our code. While our interest is mostly in the light harvesting systems, such developments will also help in describing other interesting systems. Application of the developed method to light harvesting systems, which are of interest to experimentalists, is another aspect of the project. Another goal is to study the electronic structure of light-harvesting molecular systems in an environment such as on surfaces or in the presence of spectator molecules where the effects due to morphology and polarization can be large.

FY 2014 HIGHLIGHTS

We have applied our method to two novel acceptor systems, which are being tested in the laboratories of our collaborators at UTEP and UCSB. We have shown that using trimetallic nitride endohedral C_{80} fullerene in a donor-acceptor dyad can enhance the charge transfer excitation energies by about 25% compared to C_{60} . Another application to a dye-attached fullerene showed that the linker addition site strongly influences the electronic structure of the dye-attached molecule resulting in higher electron

affinities for some of the systems. The charge transfer exciton binding energy in the dye-functionalized fullerene:P₃HT systems is lower than the corresponding value in PCBM:P₃HT system.

Theoretical Studies of Combustion Dynamics

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Funding: \$129,999 (2014)

PROGRAM SCOPE

Theoretical and computational studies of gas phase reaction dynamics of relevance to combustion. The past year has focused on energy transfer in allyl and hoco in collisions with Ar, using high-level *ab initio* potential energy surfaces in classical trajectory calculations. Mode specific tunneling in unimolecular reactions was another research area. Code development of MULTIMODE was planned. This unique code performs high-level rovibrational calculations of molecules.

FY 2014 HIGHLIGHTS

Several publications resulted from this research. Three were on the energy transfer in the allyl radical and the hoco radical in collisions with Ar atoms. The dominant role of rotational energy transfer was highlighted. These calculations also showed the limitations of the widely-used pairwise models to describe the intermolecular interactions. The tunneling lifetime of trans-hydroxymethylene to formaldehyde was shown to decrease dramatically upon excitation of the bending mode of trans-hydroxymethylene. This study made use of a new highly accurate full-dimensional potential energy surface for the cis/trans-HOCH and H₂CO parts of the full potential.

Advanced Modeling of Ions in Solutions, on Surfaces, and in Biological Environments

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Lawrence Berkeley National Laboratory
Students: 5 Postdoctoral Fellow(s), 5 Graduate(s), 0 Undergraduate(s)
Funding: \$372,130 (2014)

PROGRAM SCOPE

This proposal combines expertise from academe and National Labs to advance the state of molecular modeling of water with empirical and ab-initio techniques. Neat water and hydrated ions in situations relevant for future research applications dealing with energy and the environment will be studied. To achieve these goals community codes will be elaborated and augmented to incorporate new theoretical concepts and recent algorithmic advances. The project complements on-going experimental effort at the DOE Labs to probe water and its solutions using advanced spectroscopic techniques.

FY 2014 HIGHLIGHTS

Princeton (Car, E):

1. Car studied the ST2 model of water with advanced free energy methods finding that two metastable liquid phases and a stable crystal phase exist at the same deeply supercooled thermodynamic condition, a result with important implications for our understanding of the water anomalies (published in Nature)
2. Car showed that the collective effects of exact exchange and non-local van der Waals/dispersion interactions are crucial for predicting a microscopic structure of ambient liquid water in quantitative agreement with experiment (published in the Journal of Chemical Physics).
3. E designed new multi-scale numerical algorithms that probe the free energy landscape obtaining rather detailed understanding of the melting mechanism of simple solids (published in Science). An extension of this work to model ice melting and nucleation is underway.

Temple (Wu, Klein):

1. Wu (in collaboration with Car) studied the effect of advanced functional approximations on the structure of water (published in the Journal of Chemical Physics).
2. Wu and Klein extended this study (in collaboration with Car) to investigate how functional approximations affect the solvated water ions (hydroxyl and hydronium) and the hydroxyl radical. The progress made in describing these defect complexes has far reaching consequences on the chemistry and physics of autoprotolysis.

LBL (Ng, Yang, and Lin):

Significant progress was made in the development of the parallel pole expansion and selected inversion (PEXSI) method (<http://www.pexsi.org/>). A paper on the parallel selected inversion of large sparse matrices was submitted to ACM Trans. Math. Software. PEXSI was integrated with SIESTA for electronic structure calculations on large cells (published in the Journal of Physics Condensed Matter). Work to integrate PEXSI with CP2K is ongoing. This will allow us to perform large-scale ab-initio molecular dynamics simulations in collaboration with the Princeton and Temple teams.

Quantum Mechanical Evaluation of CZTS Photovoltaic Materials

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Funding: \$166,000 (2014)

PROGRAM SCOPE

Solar energy conversion via photovoltaics to produce carbon-neutral electricity offers tremendous promise but wide-scale deployment is impeded by a lack of sunlight absorbers that simultaneously offer high efficiency and low manufacturing costs. The novel semiconductor $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) promises both: all of its constituent elements are abundant and non-toxic; it has an ideal band gap with a large absorption coefficient; and it can be easily manufactured as a thin film by spraying suitable inks. However, CZTS is still limited by comparatively low efficiencies and difficulties synthesizing the desired crystallographic phase. We propose to use first-principles quantum mechanics methods to explore potential routes to selectively grow the preferred phase (kesterite). Excited states will be treated with many-body Green's function methods, as well as embedded correlated wavefunction (ECW) theory, to evaluate trapping propensity of defects. Off-stoichiometry surface modifications will be explored to identify compositions that improve band alignments at interfaces and reduce recombination. The CdS layer currently used in the CZTS modules is environmental unfriendly, so we will interrogate interface properties of alternative buffer layers with the aim to replace it. We also propose to search for dopants or defects that will induce intersystem crossing between singlet and slightly lower-energy triplet excited states, as the longer lifetime of the triplet states could effectively prevent recombination. We will develop our ECW theory to calculate singlet and triplet electron-hole pair, as well as charged defect states, which are difficult to study within periodic calculations. Finally, we propose to go beyond the traditional planar architecture and consider whether nanostructures could improve CZTS performance. By using these state-of-the-art techniques, we hope to contribute to the development of a cheap, abundant, and non-toxic material for efficient solar energy conversion.

FY 2014 HIGHLIGHTS

We began our work by computing effective Hubbard (U_{eff}) parameters for the 3d electrons of Cu(I), Zn(II), and Sn(IV) via our UHF-based embedded cluster methodology, which we showed was much more robust than the conventional constrained DFT scheme for closed shell metal ions. Subsequent use of these *ab initio* U_{eff} parameters within DFT+U theory accurately reproduced experimental lattice parameters and bulk moduli for relevant metal oxides and CZTS. After this validation study, we utilized this *ab initio* DFT+U approach to study the thermodynamic stability of all three phases of CZTS (kesterite, stannite and wurtzite) and most common secondary compounds. We confirmed that even though formation of CZTS itself is very exothermic, the kesterite and stannite phases of CZTS are very close in free energy. Consequently, secondary phase formation and the associated Cu/Zn sublattice disorder is very difficult to avoid. We next evaluated the cleavage energies of a variety of low-index surfaces of all phases of CZTS. We found that for a few ((100)/(001)) orientations, the desired kesterite phase has lower cleavage energies compared to the stannite phase. These "beneficial surfaces" might provide extra stability for the kesterite phase to form in nanoscale thin films. However, these beneficial surfaces are not observed during bulk synthesis, so external templates will be needed to control the growth direction of the crystal. We therefore studied interactions between a potential growth template, namely a zincblende ZnS (001) substrate, and ultrathin films of kesterite and stannite CZTS. We found significantly enhanced relative stability of the kesterite phase grown on the ZnS (001) substrate, especially in the initial stage of crystallization. We thus propose using a ZnS (001) substrate as a potential means to synthesize high-quality, single-phase kesterite CZTS thin films.

Multiscale Investigation of Thermal Fluctuations on Solar-Energy Conversion

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PROGRAM SCOPE

One source of inspiration in the quest to identify new materials capable of converting solar energy into chemical fuels is to learn from plants and bacteria about the mechanism of photosynthesis. One of these light-harvesting materials is the molecular triad that consists of a fullerene (C_{60}) that acts as an electron acceptor, a chromophore that absorbs visible light, and a carotenoid that acts as an electron donor. This charge-separated state can potentially catalyze water into hydrogen, or carbon dioxide into methane when it absorbs sunlight. However, because the molecular triad is a structurally complex molecule in solvent and its charge-separated state is transient, it is challenging to adapt a triad molecule into real-world applications. The objective is to characterize the dynamics and structures of a charge-separated triad in polar/apolar solvents by theory, modeling, and large-scale computer simulations. To achieve this objective, first I plan to develop a multiscale model that enables computer simulations to investigate the thermal effects on the optical properties of a molecular triad in solution at a sub-microsecond time scale. The major effort is to effectively coarse-grain the solvent molecules that are far away from the core region around a triad where the interactions will be evaluated quantum mechanically. Second, I aim to develop a statistical-mechanical view of the rate relaxation for a triad molecule in solution. I plan to compute the rates of relaxation from a photo-excited state to a charge-separated state on several triad structures that are dominant in solutions of varying polarities. These relaxation pathways will be weighed by the population size of these triad structures and dependent on the thermal effect and the solvent polarity. The outcome of our research is important because of a far-reaching impact on the application of solar energy conversion.

FY 2014 HIGHLIGHTS

I have been collaborating with Professor Barry Dunietz from the Kent State University to further understand the impact of structural variety of the molecular triad on its charge-transfer (CT) mechanism. It took two years of training the postdocs from each lab to learn new computational tools and developing the protocols for understanding the complexity of the triad. We successfully established the relationship of the CT kinetics and the triad conformation using both quantum mechanics calculations and molecular dynamics simulations. We computed the rate of CT at two distinctive conformations of the triad of linear and bent geometries. The linearly extended conformation, in which the donor (carotenoid) and the acceptor (fullerene) are separated by nearly 50 angstroms, enables charge separation through two sequential CT steps, following an excitation localized on the porphyrin. A representative structurally bent conformation, however, attenuates the CT, although the donor and the acceptor are spatially closer in space. Our computed rates of CT at the linear conformation are in good agreement with experimentally measured values. Our work provides a fundamental understanding of the photo-induced CT process in the molecular triad. This work was recently submitted to the PNAS (1). Dr. Balamurugan who was supported by this award accepted an offer as a Scientific Computing Consultant, at the Computation Institute, University of Chicago last summer. Dr. Oleg Starovoytov who

started in January 2015 as a postdoc will continue this line of research. He will develop and apply the polarizable force fields to the molecular dynamics simulations of molecular triad. We expect it will improve the computational outcome.

1. Manna AK, Balamurugan D, Cheung MS, Dunietz BD. Unraveling the mechanism of photoinduced charge-transfer in carotenoid-porphyrin- C_{60} molecular triad. Submitted to Proc Nat Acad Sci USA 2015.

Developing Electron-Correlated Methods for Excited State Structure and Dynamics in the NWChem Software Suite

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Funding: \$481,567 (2014)

PROGRAM SCOPE

A suite of new theoretical methods is being developed and implemented in the NWChem computational chemistry software suite in order to provide improved capabilities for excited-state dynamics in the gas phase and to add the capability to perform electronically excited-state dynamics in solution. Successful implementation will be transformative for the study of photochemical reactions with levels of accuracy similar to those commonly available for ground-state thermal reactions. Developed methods will have a broad impact as they will be implemented in a robust, widely available, actively supported software environment. The implementation will benefit from the expertise of the NWChem development team and infrastructure at the Environmental Molecular Science Laboratory and from dedicated 'guinea pig' end users. It will also benefit from the expertise of people at the SciDAC Institute for Frameworks, Algorithms, and Scalable Technologies for Mathematics (FASTMATH) and at the SciDAC Institute for Sustained Performance, Energy, and Resilience (SUPER).

FY 2014 HIGHLIGHTS

The most recent version of NWChem was released (ver 6.5). This newest release incorporates analytic time-dependent density functional theory gradients for a wide variety of functionals, the continuum solvation model based on the electron density (SMD), and the vertical electrostatic model (VEM) for the state-specific inclusion of solvatochromic effects on excited-state energies. Prior to incorporation into NWChem, significant progress has been made on coupling real-time time-dependent density functional theory with nuclear dynamics on adiabatic potential energy surfaces with plans to add non-adiabatic couplings in the future. Speed-up of key algorithms using Kernel Polynomial Methods and the Lanczos algorithm has been accomplished along with implementation of a thread-level OpenMP parallelization scheme designed more effectively to exploit future many core architectures. Progress has been made on the rapid selection of representative configurations from simulations including explicit solvent around large chromophores and the mapping of that information to a coarse-grained simulation model. Progress has also been made on paradigmatic photochemical reactions taking place on high-dimensional potential energy surfaces through efficient diabaticization and identification of privileged coordinate schemes. A new multiconfiguration pair density functional theory has been developed to extend the

range of conventional density functional theory to chemical systems characterized by high degrees of multideterminantal character.

EARLY CAREER: Multiple Coupled Potential Energy Surfaces with Application to Combustion

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Funding: \$150,000 (2014)

PROGRAM SCOPE

This project combines developments in the areas of PES fitting and multistate multireference quantum chemistry to allow spectroscopically and dynamically/kinetically accurate investigations of key molecular systems, many of which are radicals with strong multireference character and have the possibility of multiple electronic states contributing to the observed dynamics. A main goal is to develop general strategies for robustly convergent electronic structure theory for global multichannel reactive surfaces. Combining advances in *ab initio* methods with automated interpolative PES fitting allows the construction of high-quality PESs incorporating thousands of high level data to be done rapidly through parallel processing on high-performance computing (HPC) clusters. New methods and approaches to electronic structure theory will be developed and tested through applications. Some effort will be applied to the development of Quantum Monte Carlo (QMC) and working to apply these methods in the context of global PESs. The feasibility of capturing a larger fraction of the correlation energy than is possible with traditional electronic structure approaches will be tested on suitable combustion related systems. Strategies will be developed to generate QMC data in the context of a distributed high-throughput computing model in which tens or even hundreds of kiloprocessors are used.

FY 2014 HIGHLIGHTS

The high temperature spin-forbidden kinetics of the $\text{CO} + \text{O} \rightarrow \text{CO}_2$ reaction was studied using the coherent switches decay of mixing (CSDM) semi-classical trajectories method. Three coupled PESs at the MRCI/CBS level (1 singlet and 2 triplets) were constructed including geometry dependent couplings. The total rate coefficient obtained is 7–35 times larger than the values often used in combustion kinetic models. A multireference (MRCI-F₁₂) data set of ~100,000 symmetry unique points was computed for methane. A potential energy surface (PES) of benchmark quality ($r_{\text{mse}} < 1 \text{ cm}^{-1}$) was obtained using a permutation invariant PIP-IMLS scheme. The PES was confirmed (by full dimensional variational calculations) to be spectroscopically accurate in the methane well, and is now being extended to include the $\text{CH}_3 + \text{H}$ and $\text{CH}_2 + \text{H}_2$ channels for future use in dynamics studies. We worked with a developer of GAMESS to successfully interface multiconfigurational trial wavefunctions from GAMESS to the CASINO Quantum Monte Carlo (QMC) code. Some benchmark potential energy curves were computed using QMC that are comparable to high level traditional quantum chemistry and show promise for capturing large fractions of the dynamic electron correlation.

Dynamics of Peroxy and Alkenyl Radicals Undergoing Competing Rearrangements in Biodiesel Combustion

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Funding: \$80,000 (2014-2015)

PROGRAM SCOPE

The ignition of diesel fuel depends on isomerization of peroxy radicals ($\text{ROO}\bullet$) via a hydrogen shift reaction to produce hydroperoxy alkyl radicals ($\bullet\text{QOOH}$). Production of multiple OH radicals (chain branching) in the chemistry following reaction $\bullet\text{QOOH}$ production leads to autoignition. Processes such as elimination of HOO terminate the organic radical chemistry that leads to autoignition. Experimentalists face several difficulties in gaining an understanding of this chemistry, and, until 2014, no QOOH species had ever been detected by experiment! This has inspired many computational studies of these processes. Biodiesel fuel is increasingly being used worldwide. Although we have a fair understanding of the molecular details of the chemistry of peroxy radicals derived from alkanes, biodiesel fuels contain ester and olefin groups which significantly impact the thermodynamics and kinetics of biodiesel ignition. The broader goal of this research is to carry out systematic computational studies of the elementary kinetics of this chemistry for compounds that are models for biodiesel ignition. This includes not only the reactions described above, but also reactions leading from $\bullet\text{QOOH}$ to chain branching. Another aspect is that the olefin groups in biodiesel fuels lead to carbon-centered radicals that have yet another available reaction pathway. Consider a linear carbon chain with a carbon-carbon double bond and a radical centered on a carbon atom. This linear species can cyclize by forming a bond between the radical center and either one of the two carbons of the double bond. The cyclic radical thus produced can revert back to the initial, acyclic radical, or decyclize to form a branched carbon chain with a double bond and a carbon-centered radical. The formation of the branched radical changes the competition between chain branching and termination in diesel autoignition.

FY 2014 HIGHLIGHTS

Methyl butanoate (MB) is composed of a methyl ester group and a short alkyl group. MB oxidation mechanisms have been studied as the starting point for understanding biodiesel combustion for a decade. The CBS-QB3 composite method is used to determine reaction energies and activation barriers to reactions of peroxy radicals and the corresponding QOOH species. We find peroxy radical interconversions of $\bullet\text{OOQOOH}$ radicals from methylbutanoate commonly possess the lowest barriers of any unimolecular reaction of these radicals, despite that they proceed via 8-, 10- and 11-member ring transition states. At temperatures relevant to autoignition, these peroxy radical interconversions are dominant or significant reaction pathways. This means that $\bullet\text{OOQOOH}$ radicals that were expected to be produced in negligible yields are, instead, major products in the autoignition of methyl butanoate. These reactions have not previously been considered for OOQOOH from MB, and will require revision of models of autoignition of methylbutanoate and other esters. We examined exo- and endo-cyclization of a number of isomers of the straight chain unsaturated C_8H_{15} (n-octenyl) radical using the CBS-QB3 level of theory. Endo-cyclizations lead to the carbon radical center being part of the ring while exo-cyclization leads to the carbon radical center being on a substituent of the ring. The exo cyclization and

decyclization reactions are strongly favored, kinetically, over the endo cyclizations, even though the enthalpy changes for the exo and endo processes are almost identical. At combustion temperatures, it seems likely that the n-alkenyl radical could achieve quasi-equilibrium with the product of exo reactions. Moreover, the cyclization reactions seem to have lower barriers than the H-shift reactions of the same isomer. Those H-shift reactions are commonly included in detailed combustion mechanisms, but the exo- and endo-cyclization reactions are usually not included.

Electron Transport Modeling of Molecular Nanoscale Bridges Used in Energy Conversion Schemes - Transfer Balance from UM

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Funding: \$305,576 (2012-2015)

PROGRAM SCOPE

The goal of the research program is to reliably describe electron transport and transfer processes at the molecular level. Such insight is essential for improving molecular applications of solar and thermal energy conversion. We develop electronic structure models to study (1) photoinduced electron transfer and transport processes in organic semiconducting materials, and (2) charge and heat transport through molecular bridges. We seek fundamental understanding of key processes, which lead to design new experiments and ultimately to achieve systems that demonstrate improved properties.

FY 2014 HIGHLIGHTS

In one thrust, we investigate charge and heat transfer processes in molecular bridges that are candidates for thermoelectric applications. We analyzed the role of anchoring groups in the reorganization of frontier molecular orbitals (JPCL, 2013). In another project, we showed that molecular bridges can function as spin filters to actively control the heat flow using a magnetic field (PRB, 2013). In the second thrust we study photoinduced charge transfer (CT) processes through interfaces of organic semiconducting materials. We developed a fully quantum mechanical protocol to compute CT kinetics, that implements a Fermi-Golden rule picture of CT (first reported in a JPCB 2013 paper). We showed that a fully quantum mechanical scheme is necessary for reliable modeling of the CT processes, whereas the pervading semiclassical Marcus picture grossly underestimates their rates. In follow up studies we study important aspects of the molecular interfaces. For example, we show that molecular-scale means can tune the kinetics through stabilization of CT states affected by the polar environment (JCP comm, 2014). Our electronic structure approach combines charge constraint DFT and range separated based DFT to study CT properties in condensed organic materials. In a related study we investigated a high profile solvated tri-nuclear complex (two Fe and one Pt bridged centers). We find that the solvated complex differs substantially in structure from the resolved crystal one. We point out that the measured spectroscopies and indicated CT processes are substantially different than widely accepted (JACS, 2014). In an on-going collaboration with Prof. Cheung (Houston) we investigate the relationships of conformational flexibility and photoinduced CT in a molecular triad system

EARLY CARRER: First Principles Modeling of Metal-Electrolyte Systems: A Novel Approach to the Study of the Electrochemical Interface

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Funding: \$150,000 (2014)

PROGRAM SCOPE

The role of surface polarity is explored and linked to the structure of the interfacial water. In particular the research examines how ferroelectric surfaces can enhance the dissociation and deprotonation of surfaces. Project goals are to model a realistic ferroelectric/water interface, and understand: (i) The screening of polar ferroelectric surfaces by bulk liquid water. (ii) The nature of the electrical double layer formed by the water molecules while screening surfaces with different polarities. (iii) The modification of the electron and hole states at the water/surface interface. (iv) The relation between water dissociation and proton diffusion to the polar nature of the semiconductor surfaces. A second main research thrust is to model the proton affinity of polar surfaces. The acidity of a surface plays a central role in the chemical reactions happening at the water semiconductor interface. One of the main objectives of current project is to evaluate the pK_a values for polar surfaces, both oxides (ferroelectric oxides) and GaN based. This entails an initial search for surfaces with high dissociative potential, and then, among the ones found, subsequent *ab initio* molecular dynamics simulations (AIMD) at room temperature will be performed to monitor deprotonation events, together with fluctuations in local surface charges. The results of this study will allow for the evaluation of the contribution to the proton affinity of the fluctuations of the local charges at the semiconductor surface and their coupling to surface solvent fluctuations.

FY 2014 HIGHLIGHTS

A. This work is based on the use of density functional theory (DFT) to understand the effects of zero-point motion in water and ice. Water exhibits a very rich phase diagram which is partially due to protonic order-disorder phase transitions. Local density functional theory calculations have been used to evaluate the accuracy of a commonly used classical method for describing water. The latter model includes the role of polarization. After taking zero-point nuclear quantum effects, within both models, and using a quasi-harmonic approximation to determine free-energies, it has been demonstrated that the more accurate quantum-mechanical methods must be used to determine the most stable phase. The DFT approach predicts the proton ordered ice XI as the most stable phase and a predicts a phase transition at 91K. We have also analyzed the structural properties (stability and bulk modulus) of both ice phases in detail, and we have carefully studied both the isotropic and anisotropic compressibilities. The study shows a link between the isotope effects in liquid water and the compressibility anomaly of liquid water and the phase diagram of ice, and shows that nuclear quantum effects in liquid water can be used to shed light into the origin of the anomalies of both liquid water and ice.

B. Density-Functional-Based electronic structure methods have been used to predict the properties of an alloy composed of a mixture of gallium arsenide and zinc oxide. The random alloy has been generated using cluster expansion models from previous work.

Water Dissociation, Electronic Structure and Proton Diffusion Dynamics at Photo-Catalytic Surfaces

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Funding: \$157,001 (2014-2015)

PROGRAM SCOPE

The research objective of this proposal is the computational modeling of the metal-electrolyte interface purely from first principles. The accurate calculation of the electrostatic potential at electrically biased metal-electrolyte interfaces is a current challenge for periodic *ab-initio* simulations. It is also an essential requisite for predicting the correspondence between the macroscopic voltage and the microscopic interfacial charge distribution in electrochemical fuel cells. This interfacial charge distribution is the result of the chemical bonding between solute and metal atoms, and therefore cannot be accurately calculated with the use of semi-empirical classical force fields. We will study in detail the structure and dynamics of aqueous electrolytes at metallic interfaces taking into account the effect of the electrode potential. The electrode potential will be set by using the methodology already developed for the study of electronic transport in nano-structures. The *ab-initio* molecular dynamics (AIMD) simulations will be performed with the SIESTA program. An interface for the combination of both methods in AIMD simulations will be developed. Methods based on Density Functional Theory will be adapted and tuned for efficient and accurate AIMD calculation of metal-electrolyte interfaces. The PI has a well-established record of applying DFT to this problem and has already successfully developed a formalism within the Siesta program to accelerate molecular dynamics simulations of metal-water interfaces. The PI also has a broad experience in the field of electronic transport in nanostructures, with 4 high profile articles published in this area.

FY 2014 HIGHLIGHTS

We have studied the structure and dynamics of liquid water in contact with Pd and Au (111) surfaces using *ab initio* molecular dynamics simulations with and without van der Waals interactions. Our results show that the structure of water at the interface of these two metals is very different. For Pd, we observe the formation of two different domains of preferred orientations, with opposite net interfacial dipoles. One of these two domains has a large degree of in-plane hexagonal order. For Au, a single domain exists with no in-plane order. For both metals, the structure of liquid water at the interface is strongly dependent on the use of dispersion forces. The origin of the structural domains observed in Pd is associated to the interplay between water/water and water/metal interactions. This effect is strongly dependent on the charge transfer that occurs at the interface and which is not modeled by current state of the art semi-empirical force fields. *J. Chem. Phys.* 142, 034706 (2015)

Non-Adiabatic Molecular Dynamics Methods for Materials Discovery

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PROGRAM SCOPE

The rate of breakthrough discoveries in energy-related materials sciences depends crucially on our ability to predict and control non-adiabatic transitions between electronic states. For example, efficient sensitizer dyes for solar cells should exhibit large transition probabilities from the initial absorbing state to the charge-injecting state and minimal losses through other decay channels. Non-adiabatic molecular dynamics (NAMD) simulations are the method of choice to attack these problems. However, predictive NAMD simulations are extremely demanding, and the theoretical and the computational machinery to tackle non-adiabatic processes in real materials is woefully inadequate. The goal of this project is to provide robust, predictive, and broadly applicable computational tools enabling NAMD simulations in real materials with unprecedented accuracy and realism. We are well on our way to developing a general-purpose code enabling 10-100 picosecond ensemble NAMD simulations for molecules and nano-sized clusters with 100 or more atoms at the level of hybrid time-dependent density functional theory (TDDFT). Our implementation uses atom-centered Gaussian basis sets and rigorously treats non-adiabatic couplings between all relevant states. Tully's fewest switches surface hopping algorithm is to be employed for nuclear dynamics. The availability of these tools will dramatically accelerate the discovery of new energy-related molecular materials. We are combining the latest developments in excited state methods, response and analytical derivative theory, functional development, and sampling methods with efficient iterative algorithms and parallel computing, including acceleration by graphics processing units. The code developed in this project will be rapidly and widely distributed through the Turbomole package, and parts have already been released. We are validating our methodology by comparison to accurate experiments and calculations.

FY 2014 HIGHLIGHTS

A highlight in FY 2014 was the development of improved iterative subspace algorithms for large-scale response calculations which lie at the heart of materials simulations. The simple but effective idea underlying this method is to exploit the reduction of the residual norms as convergence is reached. The method is particularly successful when Coulomb and exchange portions of the linear response equations are separated and in combination with fast factorization techniques such as the resolution-of-the-identity (RI) approximation. Up to five-fold speedups were observed in TDDFT calculations, with larger benefits for larger systems. This significantly extends the scope of NAMD simulations, where solution of the TDDFT response equations is a rate-determining step. Another important accomplishment was the extension of TDDFT-based NAMD simulations to open-shell systems. This has enabled us to tackle homolytic bond breaking, which is very common in photochemical reactions. Previously, homolytic dissociation could only be addressed by multi-reference calculations, which are limited to molecules with few atoms. The present developments make it possible to obtain a qualitatively complete picture of photochemical reactivity for systems with up to 100 atoms for the first time. Finally, we have completed the derivation and a first implementation of first-order non-adiabatic couplings between two excited states in the hybrid TDDFT framework. The result is consistent with time-dependent response theory, but also reveals an incorrect pole structure of the quadratic TDDFT response within the adiabatic (zero frequency) approximation for the exchange-correlation kernel. This result highlights the importance of frequency-dependent kernels for NAMD simulations. In the meantime, an approximate version of the couplings that becomes exact at conical intersections is the most promising candidate for applications.

Nanoporous Materials Genome: Methods and Software to Optimize Gas Storage, Separations, and Catalysis

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Jeffrey Neaton; Lawrence Berkeley National Laboratory
Wendy Queen; Lawrence Berkeley National Laboratory
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Funding: \$1,770,000 (2014)

PROGRAM SCOPE

The Nanoporous Materials Genome Center (NMGC) discovers and explores microporous and mesoporous materials, including metal-organic frameworks (MOFs), zeolites, and porous polymer networks (PPNs). These materials find use as storage and separation media and catalysts in many energy-relevant processes and their next-generation computational design offers a high-payoff opportunity. Towards that end, the NMGC develops state-of-the-art predictive modeling tools, databases, and web-based repositories, and employs them to increase the pace of materials discovery. The goals of the NMGC are advanced by a tight collaboration between leading experimental groups in the synthesis and characterization of nanoporous materials and of computational groups with experience in molecular simulation, electronic structure calculations, and theory. The majority of the completed projects resulted from iterative feedback where computational modeling was instrumental for understanding the function of specific nanoporous materials or for discovering materials with optimal properties for subsequent synthesis.

FY 2014 HIGHLIGHTS

The NMGC research efforts have already led to more than 40 publications. Here, we highlight the key achievements of five application projects and one web tool that are central to the goals of the NMGC.

- a. The computation-ready, experimental (CoRE) MOF database contains ~5000 porous structures that are derived from experimentally refined crystal structures by removing solvent molecules and

- resolving partially occupied or disordered atoms. The CoRE MOF database is utilized to find materials for methane storage and hexane isomer separation.
- b. A computational methodology is developed that applies known chemical transformations for in silico synthesis of organic linkers to identify MOFs with high methane deliverable capacity.
 - c. Enabled by a multistep screening workflow, efficient sampling algorithms, accurate force fields, and a parallel execution hierarchy utilizing up to 131,072 compute cores on Mira at Argonne, we identify zeolites with exceptional selectivities for ethanol purification from aqueous solution and the transformation of alkanes with 18-30 carbon atoms.
 - d. Enzymatic heme and non-heme high-valent iron-oxos are known to activate very strong C–H bonds; we demonstrate that a MOF featuring site-isolated iron centers in a weak-field ligand environment can convert ethane into ethanol and acetaldehyde using nitrous oxide as the terminal oxidant and elucidate all steps in the mechanism.
 - e. We use quantum mechanical computations to identify a new MOF with open vanadium sites that is of potential utility for the separation of dinitrogen from other light gases and reveal that two types of interactions, the σ donation and π^* backbonding, are responsible for the strong V-N₂ bond. In collaboration with the Materials Project, the NMGC has developed the Nanoporous Materials Explorer. This openly accessible web-based tool aids materials discovery and also serves as repository for computational and experimental data generated by the NMGC.

EARLY CAREER: Many-body Effects in Transport and Energy Transfer

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Funding: \$152,400 (2014)

PROGRAM SCOPE

Understanding dynamics of systems interacting with baths is crucial in developing memory and logic molecular devices, molecule based sensors, photovoltaics for solar conversion, and optoelectronics. Strongly correlated resonant inelastic electronic transport is particularly relevant for application purposes. Sensitivity of molecular electronic and vibrational structures to oxidation/reduction/excitation calls for the development of approaches capable of treating molecular response in the language of many-body states, in contrast with the effective single-particle formulations employed in most *ab initio* schemes today. My goal is to formulate a truly non-equilibrium many-body theory capable of retaining universality and exactness of scattering theory in the treatment of on-the-bridge interactions, which will retain junction information, and will allow to incorporate sophisticated methods of equilibrium quantum chemistry and molecular spectroscopy in the transport calculations. Another important goal is to introduce non-adiabatic molecular dynamics (in particular, fewest-switches algorithm of the surface-hopping method) into molecular junction setup. The proposed research considers fundamental problems of molecular transport theory with potential impact on possible technological applications. Proposed theoretical developments are of multidisciplinary nature – the consideration encompasses problems and methods of quantum chemistry, computational and many-body physics, non-equilibrium statistical mechanics, and molecular spectroscopy. Within the proposed approach, the non-equilibrium state of the system is described in the language of molecular states. This means that all on-the-molecule correlations are taken into account from the very start, and that well developed methods of quantum

chemistry and equilibrium molecular spectroscopy can be employed for description of transport and optical response of molecular devices.

FY 2014 HIGHLIGHTS

We focused on the development of methods of the nonequilibrium atomic limit and on their application to transport and optical response of molecular junctions.

1. Methods development for the nonequilibrium atomic limit:
 - a. An invited feature article was published [A. J. White *et al.*, *J. Phys. Chem. C* 118, 11159-11173 (2014)] reviewing the methods developed within the project and their applications to model and ab initio simulations
 - b. A paper on PO-NEGF EOM method was published [M.A.Ochoa *et al.*, *J. Phys.: Condens. Matter* 26, 455301 (2012)], where solid methodological proof of viability (something which was questioned in the literature) of the Hubbard NEGF approach was presented.
2. Molecular optoelectronics: A first many-body approach to Raman spectroscopy in open nonequilibrium devices within the PP-NEGF (one of the methods of the nonequilibrium atomic limit) was formulated and applied to describe within ab initio simulation experimentally observed shift in position of the Stokes line under bias [A. J. White *et al.* *Nano Lett.* 14, 699-703 (2014)].
3. Quantum interference and coherent control in junctions: Preferability of the methods of the nonequilibrium atomic limit for describing processes involving coherent transfer of both charge and energy was demonstrated in a publication [A. J. White *et al.*, *Phys. Rev. B* 205424 (2013)]. We employed the PP-NEGF in a search for measurable effects in combined coherent charge and energy transfer in molecular junctions. In particular, inspired by the known charge and spin fluxes separation effect, we demonstrated that tuning parameters of the external laser field (amplitude and/or frequency) lead to coherence-induced spatial separation of charge and energy (electron excitation) fluxes in multi-terminal molecular junctions. Note that this observation may be relevant also for a technically similar consideration of propagation of vibrational excitation in junctions and hence to constructing low-heating molecular devices.

EARLY CAREER: Interfacial Electrocatalytic Processes from First Principles

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Funding: \$150,000 (2014)

PROGRAM SCOPE

This program develops and applies electronic-structure based methods to the study of electrocatalytic processes at solid/liquid interfaces. We are simultaneously pursuing two general goals: a) the development of detailed electrocatalytic reaction mechanisms for electrochemical denitrification processes, an effort in which we are adopting techniques from electronic structure analyses of traditional heterogeneous catalytic reaction processes to complex electrocatalytic environments, and b) the optimization of electronic structure methods to treat the structural and catalytic complexity found at multifunctional metal/oxide interfaces in alkaline electrochemical environments. Both efforts also

involve use of ab-initio molecular dynamics simulations to describe the structure of water near the electrocatalyst surfaces.

FY 2014 HIGHLIGHTS

We have determined the elementary reaction mechanisms of electrochemical denitrification, a process that is of importance for purification of biologically-contaminated wastewater streams and that also serves as a model system on which to develop appropriate computational techniques. We have considered reduction of NO to N₂O, NH₂OH, and ammonia on different single crystal platinum surfaces and have identified new mechanistic pathways for these conversion processes, including the formation of a previously unknown trans dimer of NO that serves as a precursor to N₂O formation. We are in the process of generalizing these results to produce predictions of both NO and nitrate reduction kinetics over a variety of transition metal alloy surfaces, with an ultimate goal of developing a general, systematic toolkit of techniques to permit the rapid and efficient elucidation of complex reaction networks on similar metal surfaces. Additionally, we have developed an approach to accurately describe the oxidation state and geometric structures of thin (1-2 ML) oxyhydroxide films on precious metal substrates, and we have, for the first time, related the detailed structural characteristics of these films to their electrocatalytic activity for hydrogen production in alkaline solutions. The results have revealed a complex and stimulating interplay between the local geometric structure, the oxidation state, and the electrocatalytic activity.

Quantum Dynamics of Elementary Chemical Reactions

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Funding: \$120,001 (2014)

PROGRAM SCOPE

The goal of this grant is to develop theoretical and computational methods that will allow us to understand the dynamics of gas phase bimolecular reactions, particularly those involved in combustion.

FY 2014 HIGHLIGHTS

The focus of our research was on the reactions between H₂O and several atomic species such as F, Cl, and O(³P). In order to understand the reaction dynamics of these prototypical tetra-atomic systems, we have constructed highly accurate potential energy surfaces from large numbers of high-level *ab initio* data over a large configuration space. The resulting full-dimensional global potential energy surfaces allowed us to carry out full-dimensional quantum dynamical and quasi-classical trajectory calculations. Mode specificity and product state distributions shed valuable light on the reaction dynamics. A good example of our work is the photodetachment of FH₂O⁻, which is published in Science in 2014. In collaboration with Bob Continetti at UCSD, we provided theoretical insights into the photoelectron-photofragment coincidence spectra, which sheds valuable light on the transition state and the post-reaction hydrogen bonded well of the potential energy surface.

Development of Accurate and Affordable Electronic Structure Methods for the Condensed Phase

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Funding: \$148,205 (2014)

PROGRAM SCOPE

The goal of this project is to develop fragment-based electronic structure methods to facilitate efficient and accurate condensed-phase *ab initio* calculations. By exploiting the 'embarrassingly parallel' nature of fragment-based approaches, these methods will leverage the power of massively-parallel computer architectures to reduce wall clock times dramatically, relatively to conventional electronic structure algorithms. As compared to other efforts along these lines, our approach is distinguished by a focus on achieving consistent, sub-kcal/mol accuracy with respect to the best available benchmark calculations. The initial stages of this project focus on non-covalent interactions (molecular clusters, aggregates, and liquids), that is, systems that suggest a very natural fragmentation pattern based on molecular monomer units. This strategy will allow us to isolate and evaluate what is necessary to achieve high accuracy in intermolecular interactions, without introducing errors due to the need to fragment the system across covalent bonds. In later stages of the project, we will attack macromolecular problems where fragmentation across covalent bonds is necessary; in these cases, we will employ a novel overlapping-fragment scheme developed previously in the PI's group. Excited states in molecular aggregates, in which the excitonic wave function is delocalized across multiple chromophore units, will also be addressed. Ultimately, this work will facilitate calculations at 'chemically accurate' levels of theory in systems of unprecedented size, harnessing the power of parallel computing in conjunction with physics-based fragmentation approximations.

FY 2014 HIGHLIGHTS

We continue our development of the 'extended' version of symmetry-adapted perturbation theory (XSAPT). XSAPT extends the traditional SAPT approach, in a naturally parallelizable way, and thus facilitates affordable calculations of intermolecular interactions in non-covalent assemblies. Using 'tuned' long-range corrected density functionals, we have shown that (contrary to conventional wisdom), Kohn-Sham orbitals can be used directly in (X)SAPT calculations without ill effects, and this provides a low-cost means to introduce monomer electron correlation into SAPT calculations. An efficient atomic-orbital implementation of (X)SAPT has been developed, which reduces the memory footprint of the algorithm and facilitates calculations on systems where the monomer units are quite large, e.g., a C₆₀ buckyball bound to an even larger molecule, or various fragments of graphene (e.g., coronene). Whereas we had previously benchmarked XSAPT only against high-level *ab initio* calculations, we are now benchmarking against experimental enthalpies and (in conjunction with simple entropic corrections) against experimental free energies of association, for difficult systems including room-temperature, solution-phase ionic complexes. Preliminary results are still of sub-kcal/mol accuracy. We have also begun to address the relative conformational energies of macromolecules (fragmenting across covalent bonds), using a two-body expansion after tessellating the system into overlapping fragments. These results suggest that we can accurately reproduce supersystem conformational energies across isomers spanning an energetic range of more than 100 kcal/mol, using

subsystem calculations no larger than 20-30 atoms. Finally, we have introduced an *ab initio* version of the Frenkel-Davydov exciton model, an approach that holds great promise for understanding excitonic energy transfer in molecular aggregates.

Breakthrough Design and Implementation of Electronic and Vibrational Many-Body Theories

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Funding: \$390,000 (2014-2016)

PROGRAM SCOPE

The goal is to develop novel many-body theories and algorithms that are systematically accurate, diagrammatically size consistent and thus applicable to molecules of all sizes and solids, capable of describing electronic and vibrational structures at zero and nonzero temperatures and chemical potentials, and scalable with respect to both the number of particles and the number of processors. We aim at solving the following three specific problems:

- (1) Finite-temperature full configuration interaction. We will formulate, implement, and test finite-temperature FCI. Here, the target quantity is no longer the energy eigenvalue of the Schrödinger equation, but the canonical and grand-canonical electronic partition functions. It serves as the benchmarks for finite-temperature many-body perturbation and coupled-cluster methods.
- (2) General-order, relativistic Monte Carlo MP2. MC-MP2 simultaneously achieves parallel scalability, negligible memory consumption, capacity to directly compute molecular properties (often difficult with QMC), and near-linear size dependence of cost even in small molecules. We will automate the generation of diagrams, their algebraic interpretation, and code synthesis. They will be combined with a Dirac–Hartree–Fock reference wave function to account for relativistic and correlation effects.
- (3) Monte Carlo size-extensive vibrational self-consistent field (MC-XVSCF) and vibrational MP2 (MC-XVMP2). We will explore a stochastic evaluation of anharmonic frequencies and zero-point energies with the size-extensive version of VSCF and VMP2 developed in this project. We will thus eliminate the expensive, non-scalable step of high-rank force constant calculations.

FY 2014 HIGHLIGHTS

We have essentially completed the proposed developments of both Monte Carlo XVSCF and Monte Carlo XVMP2 methods. The latter has been reported in J. Chem. Phys. and the former under review by J. Chem. Phys. They, along with their deterministic counterparts, are summarized in an invited review, which is under consideration by Int. Rev. Phys. Chem. Furthermore, we realized that a normal-ordered Hamiltonian for molecular vibrations, which underlies both of these methods, is hardly discussed in the literature. We, therefore, reported such a Hamiltonian, which we consider to be fundamental progress in equilibrium quantum dynamics. The development of a diagrammatic theory of vibrational coupled-cluster (XVCC) methods is underway. We continue to make significant advance in a novel algorithm of MP2 for electrons. Specifically, we have developed a stochastic algorithm of the explicitly correlated MP2 or MP2-F12 in collaboration with Professor Edward F. Valeev and his postdoctoral researcher, Dr. Jinmei Zhang, of Virginia Tech. This work has been published in J. Chem. Phys. as a Communication. An

important reason why we base our developments on the MP methods is their size consistency. In a Theor. Chem. Acc. paper, we put forth a conjecture of mutual exclusion between size consistency and variability. This paper has produced a strong reaction in a recent conference presentation. During March-September 2014, 9 papers have been published or submitted with support of this grant.

Elucidating positive quantum effects for efficient energy and charge transfer dynamics in soft solar energy conversion systems

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PROGRAM SCOPE

Fast and directed migration of excitons and charge carriers across 100 nanometer or larger length scales in soft environments is an issue of fundamental importance in developing efficient biomimetic or organic solar energy conversion devices. The primary goal of PI's research is to identify and understand novel and robust quantum effects making significant positive contribution to such exciton and charge flow dynamics. This is pursued through application of theories developed by PI's group, which can account for important quantum effects that have not been well addressed before, while also making thorough theoretical investigation of the effects of molecular level factors and the disorder. Applications are being made to generic model systems, models of photosynthetic light harvesting complexes, and to organic conjugated molecular systems in collaboration with experimental groups. Outcomes of these efforts will provide new theoretical insights, help more quantitative and reliable interpretation of spectroscopic data, and can ultimately contribute to experimental realization of efficient and robust solar energy conversion devices.

FY 2014 HIGHLIGHTS

- i. Major effort during this funding period was devoted to theoretical investigation of the photosynthetic light harvesting 2 (LH2) complex of purple bacteria. LH2 is an efficient natural excitation energy carrier with high fold symmetry (N=8-10), but the molecular level design principle governing its functionality is unknown. The PI's group has constructed an all-atomistic model of a natural LH2 based on reported X-ray crystal structure (N=9), and also constructed non-natural analogues with different fold symmetries (N=5-8 and 10-12). Molecular dynamics (MD) simulations of these models confirmed that all complexes can be formed and remain stable. However, distinctively different features were observable for different sizes in their final structures. Close examination of bonding characteristics revealed that the main source of such difference is the variation in the pattern of the hydrogen bonding (HB) between the pigment molecule and protein residues. Stable and consistent formation of HB is possible only near naturally occurring sizes (N=9,10), leading to significantly smaller disorder than non-natural ones. Simulation of the exciton transfer dynamics between two LH2s based on a recently developed theoretical approach called generalized master equation for modular exciton density (GME-MED) clearly demonstrated that the average inter-LH2 exciton transfer rates are close to the maximum for N=9 and 10. These results suggest that natural sizes of LH2 have been indeed optimized for the maximum inter-LH2 exciton

transfer rate, for which formation of stable HB and quantum delocalization of the exciton plays a critical role.

- ii. The effects of quantum environments on charge transport were studied for a one dimensional chain with energetic Gaussian disorder. Time dependent variances of populations were calculated by solving the master equation numerically. The results show the importance of using reliable quantum rate expressions for quantitative modeling.

Design of Stratified Functional Nanoporous Materials for CO₂ Capture and Conversion

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Funding: \$266,000 (2014-2015)

PROGRAM SCOPE

Efficient capture and conversion of carbon dioxide from various emission sources into valuable chemicals could be accomplished with highly tailored multi-functional catalytic sorbent materials. We utilize first-principles computational methods to investigate the fundamental interactions between carbon dioxide and hydrogen with functionalized nanoporous materials with the ultimate goal of designing materials for selective capture and reaction of carbon dioxide with hydrogen to produce chemical feedstocks or fuels. We initially focus on the simplest reduction reaction to produce formic acid from a two-electron reduction with hydrogen. We study metal organic frameworks (MOFs) as a catalytic platform for these reactions because they can be readily functionalized with a wide variety of chemically active functional groups. We initially study UiO-66 as a candidate MOF due to its high chemical and thermal stability and because it can be functionalized post-synthetically to imbue it with catalytic properties. We target Lewis acid and base sites as potential catalytic functional groups for binding and chemically activating both hydrogen and carbon dioxide. We primarily use periodic density functional theory to identify the catalytic pathways for carbon dioxide reduction within functionalized MOFs. We are able to screen different functional groups and develop predictive relationships through characterizing the properties that control binding energies and transition state geometries and energetics. We examine a variety of different chemical descriptors using computational methods in order to characterize the key properties that control the binding energy, reaction pathway, transition state energetics, and product states of the reaction. These descriptors include atomic charges, frontier orbitals, acidity, basicity, d-band centers, and electronegativity. Our calculations can ultimately be used to guide experimental synthetic efforts to design materials.

FY 2014 HIGHLIGHTS

We have designed and evaluated a variety of different Lewis pair moieties for binding carbon dioxide and heterolytically dissociating molecular hydrogen within the functionalized pores of UiO-66. The idea of using a functional group with both Lewis acid and Lewis base site on the same moiety is inspired by recent work with frustrated Lewis pairs used in solution chemistry. Our calculations show that Lewis pairs that are covalently bound to sites within a MOF retain their chemical activity for chemically binding carbon dioxide and heterolytically dissociating hydrogen even though they are not sterically hindered. We have demonstrated that the geometric constraint of being bound to the MOF makes steric

hindrance unnecessary. We have computed the reaction pathways for carbon dioxide reduction with hydrogen on several different Lewis pair functional groups bound within UiO-66. We have identified 1-(difluoroboranyl)-4-methyl-1*H*-pyrazole as the best Lewis pair functional group out of nine different groups we have screened. The reaction with this material proceeds with low barriers to produce HCOOH when hydrogen is first chemically activated by the Lewis pair in the pore. Carbon dioxide then reacts with the activated H atoms, the hydridic hydrogen binding to carbon and the protic hydrogen binding to one of the oxygens, in a single step concerted reaction resulting in a two-electron reduction. We have demonstrated that the MOF serves to reduce the reaction barrier relative to the gas phase reaction on the same Lewis pair. We ascribe this additional catalytic effect to the geometric constraint of the MOF pore, making the interaction between the activated hydrogens and carbon dioxide more favorable due to the binding of carbon dioxide to the pore walls. In this way, the functionalized MOF mimics a complex enzyme by bringing two substrates together to form an activated complex.

Electronic Structure of an Organic/Metal Interface: Pentacene/Cu(110)

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Funding: \$119,905 (2014)

PROGRAM SCOPE

Organic molecule adsorption on metal substrates is of continuing interest as thin films and self-assembled monolayers open the way toward functionalization. Interaction of small hydrocarbons with transition metal surfaces has been extensively studied by surface science methods to gain a fundamental understanding of problems relevant to heterogeneous catalysis. We have also witnessed intense efforts to employ organic molecules as the basic components in electronic devices for molecular electronics with the hope that they become an alternative to the available technology. So far, organic molecules have demonstrated the ability to be used as functional units in such devices as diodes, photo-voltaics, molecular switches, and field-effect transistors. Describing accurately the atomic and electronic characteristics of the interface between organic materials and metal surfaces is the main purpose of the present proposal. In recent years, evaluating the effect of van der Waals (vdW) forces for many physical systems, including the adsorption of small organic molecules on metal surfaces became possible thanks to the continuous improvements in vdW density functional theory (DFT). In my work, I employ a self-consistent implementation of the vdWs effects to DFT, namely the vdW-DF. I evaluate the performance of various vdW functionals by examining the equilibrium adsorption geometries and energies, and comparing the results with those available experimental and computational data. I also extract valuable information for determining the performance of organic devices. Such information includes charge transfer and charge redistribution at the interface, changes in the work function, interface dipoles and interface electronic states. I study a variety of molecules on several metal surfaces with different orientation and chemistry. Molecules such as acenes, thols and others with CN groups are studied on transition metal surfaces with orientations (111), (100), (110) and vicinals.

FY 2014 HIGHLIGHTS

I have continued my research on assessing the role of van der Waal (vdW) interactions on a variety of molecules and substrates (benzene, thiophene, sexithiophene, 1,4-benzenedimethanethiol (BDMT), 9,10-anthracenedicarbonitrile (DCA), and a cyano-substituted triarylamine (HBQUAT)). I also included van der Waals interactions in 2D materials such as silicene, the counterpart of graphene. The goal of these studies is first to assess the accuracy of the newly developed vdW functionals within the density functional theory for molecular adsorption characteristics on varying substrate chemistries, and coordination. This information will then help to extract the transferability, strengths, weaknesses of the available functionals, and provide insights into the development of new vdW functionals. Some of the work is also performed in collaboration with experimentalists. The specific work done during the reporting period between October 1st 2013 and September 30th 2014 includes (all the work is done using density functional theory with the inclusion of vdWs effects):

- 1) Adsorption characteristics of a sexithiophene molecule on Ag(110): JCP 140, 144703 (2014)
- 2) Adsorption characteristics of a thiol molecule on Cu, Ni and Pd (100): paper in preparation.
- 3) Adsorption characteristics of BDMT on Au(111): paper submitted to JPCC
- 4) Adsorption characteristics of benzene on Cu, Au, Ag, Ni, Pd, Pt, and Rh (110) surfaces: paper accepted for publication at JPCC.
- 5) In-Depth Atomic Structure of the Pentacene/Cu (110) Interface in the Monolayer Coverage Regime: Theory and X-ray Diffraction Results: JPCC 118, 27815 (2014)
- 6) Atomic and electronic structures of the sqrt(13) R13. 9° of silicene sheet on Ag (111): App. Surf. Sci. 303, 61 (2014)
- 7) Cyano-Functionalized Triarylamines on Coinage Metal Surfaces: Substrate Influence on Molecular Self-Assembly: to be submitted to Chem. Eur. J.

Dynamical Analysis of Highly Excited Spectra

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Funding: \$150,000 (2014)

PROGRAM SCOPE

Highly excited vibration-rotation dynamics of small molecular species, including those approaching the threshold of reaction, are crucial to understanding fundamental processes important for combustion. Our goal is to develop theoretical tools to analyze spectra and dynamics of these highly excited systems. A persistent theme is the use of effective spectroscopic fitting Hamiltonians to make the link between experimental data and theoretical dynamical analysis. There are three areas currently under investigation:

- 1) The role of bifurcations and the “birth of new modes in bifurcations from the low energy normal modes.”
- 2) A more recent focus has been systems approaching and undergoing intramolecular isomerization reactions. We have been developing new generalizations of the effective Hamiltonian, called “polyad-breaking Hamiltonians,” to deal with spectra of isomerizing systems. In our most recent

work we have extended these investigations to consider time-dependent dynamics, including the isomerization process.

- 3) Most recently, in a new development in our research program, we have begun an investigation of the “quantum thermodynamics” of a small quantum molecular system immersed in a quantum heat bath.

FY 2014 HIGHLIGHTS

(1) CRITICAL POINTS BIFURCATION ANALYSIS OF EFFECTIVE SPECTROSCOPIC HAMILTONIANS. In a project conducted with Dr. Vivian Tyng, we are completing our first bifurcation analysis for a rotation-vibration effective Hamiltonian, using a recent spectroscopic Hamiltonian for CO₂ fit to experimental data. We have in hand the successful critical points analysis of rotation-vibration dynamics of CO₂ on the effective Hamiltonian fit to experimental data. The analysis gives relatively simple, intelligible dynamics, comparable to but significantly extending what has been obtained with pure vibrational dynamics. At J = 0 there is only the bifurcation tree of normal modes and Fermi resonance modes. Then, as J increases, we find a principal 'Coriolis mode' that bifurcates out of one of the Fermi resonance modes at very low J, with further finer branching of the tree into Coriolis modes with increasing J.

(2) GENERALIZED SPECTROSCOPIC HAMILTONIAN FOR ISOMERIZING SYSTEMS WITH POLYAD BREAKING. This work has been primarily in collaboration with Dr. George Barnes. The recent focus of our work is systems approaching and even surmounting an isomerization barrier, in which the standard effective spectroscopic Hamiltonian breaks down. The Hamiltonian used in virtually all existing spectral fits invokes an approximate conserved quantity known as the polyad or total quantum number. In a recent step we showed that it is possible to construct an effective Hamiltonian to encompass multiple potential energy minima in an isomerizing system. As our exemplar, we used one of the most important elementary combustion species is the hydroperoxyl radical HO₂. A new direction will involve combining the existing bifurcation analysis of our HO₂ effective Hamiltonian with our thrust into entangled system-environment dynamics outlined briefly at the end of the following section.

Combining Novel Simulation Methods and Nucleation Theory to Uncover the Secrets of Gas Hydrates

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Funding: \$158,159 (2014)

PROGRAM SCOPE

First-order phase transitions modulate material properties. Nucleation and growth of a new phase proceeds through a sequence of states with coexisting phases, which are difficult to sample with conventional computer simulation methods. The usual choice of temperature as the control variable is poor, since diverse coexisting states have the same temperature. The project aims to develop and exploit our generalized replica exchange method (gREM), which specifically targets coexisting states, to obtain a new capability of characterizing first-order transitions. We propose a unified approach of gREM simulation, combination of data from different replicas with a non-iterative method we have developed, and a description of the transition via the entropy as a function of enthalpy, the control variable. The

immediate target is gas hydrates, substances of great importance for energy and climate science. In forming hydrates from methane and liquid water, the gREM robustly samples coexisting states at all stages of growth. The mechanism and phase diagram of hydrate formation is under investigation and the action of hydrate inhibitors will be considered. All coexistence involving solid/liquid water is relevant and computationally challenging, and we seek a description with the gREM for stable hexagonal ice and for the metastable β -ice which holds guest molecules in hydrates. The methods developed will advance the study of any material properties influenced by phase transitions, e.g. for nano catalysts surrounded by a lipid envelope with a solid/liquid transition.

FY 2014 HIGHLIGHTS

The theory of constant pressure molecular dynamics algorithms sampling generalized, non-Boltzmann ensembles was derived and our generalized replica exchange method (gREM) was optimized accordingly. A complete test of our approach to first-order transitions was performed, for melting of the methane hydrate scaffolding, β -ice. The states with coexisting phases were sampled, with every structural change identified with a feature in the entropy as a function of enthalpy. The position of a prominent plateau in the statistical temperature, the inverse of the enthalpy derivative of the entropy, was presented as a novel estimator of the equilibrium transition temperature. The upper spinodal gave the limit of superheating, and the Gibbs free energy profile yielded the β -ice/liquid surface tension for the first time, 26.3 mJ/m^2 . A similar new view of the equilibrium of stable hexagonal ice and liquid water was obtained. The pathway of methane hydrate formation from a dilute solution was investigated, using new methods to identify empty and partial hydrate cages. The sequence, with decreasing enthalpy, is: methane solution, piece of perfect hydrate in water, hydrate surrounded by β -ice in water, and hydrate in hexagonal ice. We believe that the catalysis of a relatively large region of β -ice by a small piece of hydrate is a key element of the growth pathway: the empty cages will be filled as more methane becomes available. The basic concept of the gREM was validated by facile observation of coexisting states in several systems.

Magnetic and Tunable Band Gap Cluster Building Blocks for Novel Nanostructure Materials and Electron Transport through their Assemblies

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Funding: \$360,000 (2014-2016)

PROGRAM SCOPE

An important development in nanoscience is the possibility of designing nanoscale materials with chosen atomic clusters as the building blocks. Since the properties of small clusters are found to change with size and composition, such an approach offers the promise of making materials with selected properties. Our DOE program proposes to undertake a comprehensive approach starting from studies of electronic structure and magnetic properties (including magnetic anisotropy energy) of free and supported clusters for identifying magnetic motifs with stable magnetic order and varying band gaps, to investigation of the transport properties of molecules of such motifs, and exploration of synthesis and

properties of larger assemblies of such motifs. The program involves four interrelated areas of study, namely:

- A. investigation of the magnetic anisotropy in free TM_nC_m/TM_nSi_m (TM = Cr, Mn, Fe, Co, Ni) clusters and in TMn clusters supported on Graphene motivated by our preliminary findings of high magnetic anisotropy in such systems;
- B. studies of metal chalcogenide superatoms and Si_nTM_m (TM = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ru, Rh, Pd) clusters to identify potential semiconducting magnetic building blocks.;
- C. studies of ligated cluster assemblies and supported ligated clusters to explore magnetic assemblies with tunable band gaps.;
- D. development of computational codes to carry out electronic transport studies that incorporate the effect of excess charge, spin ordering and anisotropy. Thereafter, building on our recent collaborations with experimental groups involved in synthesizing nanoassemblies using wet chemical methods, we will work to form similar assemblies of magnetic motifs. The research promises a class of nanoscale materials with potential applications in spintronics and other areas.

FY 2014 HIGHLIGHTS

We had a very successful period where we studied the stability of magnetic motifs that could form the building blocks of novel nanoscale magnetic materials and the emergent properties of such assemblies. Our investigations on Ag_nV^+ clusters (JACS 136, 8229 (2014)) focused on the evolution of bonding and spin magnetic moment in metal clusters while our studies on CrSi₁₂ (J. Phys. Chem. Lett. 118, 8314(2014)) examined the applicability of the 18-electron rule, currently used to account for its stability. We showed that the cluster does not conform to this rule. We are currently developing revised electronic and geometric rules for these classes of clusters. Efficient control of magnetic anisotropy and orientation of magnetization are of central importance for the application of nanoparticles in spintronics. Conventionally, magnetization is controlled directly by an external magnetic field or by an electric field via spin-orbit coupling. We demonstrated (APL 105, 152409(2014)) a different approach to control magnetization. We first showed that the low magnetic anisotropy of a Co₅ cluster can be substantially enhanced by attaching benzene molecules due to the mixing between p states of C and the d states of Co sites. We then showed that the direction of magnetization vector of a Co₅ sandwiched between two benzene molecules rotates by 90 degrees when an electron is added or removed from the system providing a new approach to control the direction of magnetization. Finally, we participated (J. Phys. Chem. 118, 8314(2014)) in the synthesis, isolation, and characterization of the ligand-protected bimetallic cluster, $Ag_4Pt_2(DMSA)_4$ (DMSA=meso-2,3,-dimercaptosuccinic acid) using wet chemical methods where our theoretical studies suggest that the Pt atoms have square planar configuration with a larger crystal field splitting of 5d orbitals than the corresponding 3d orbitals in a similar Ni based assembly. This leads to an optical spectrum that is blue shifted than for Ni.

Quantum Monte Carlo Calculations of Chemical Binding and Reactions

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Funding: \$360,000 (2014-2016)

PROGRAM SCOPE

The auxiliary field quantum Monte Carlo (AFQMC) method developed by the PIs has been shown to provide the most accurate description of strongly correlated electronic systems, from molecules to solids. Unlike other explicitly many-body approaches, QMC scales as a low order polynomial of systems size, similar to mean-field methods such as density functional theory (DFT). Since the AFQMC algorithm has the form of an entangled ensemble of mean-field calculations, it is significantly more expensive than traditional DFT calculations. This creates a bottleneck for applications to extended systems, such as large molecules and solids. One principal objective of this proposal is to develop new AFQMC computational strategies to achieve improved scaling with system size, using downfolding and localization schemes, without sacrificing the predictive power of the calculations. A second goal is to extend the reach of AFQMC to calculate excited states. The project will first be focused on building this computational infrastructure. We will implement quantum chemistry localization methods in both the occupied and virtual sectors. Then as our first application we will carry out calculations of the chemistry of two-dimensional layered transition metal dichalcogenide nanosheets, which have possible applications in a variety of fields, including catalysis, energy storage, sensing and electronic devices. The development of this theoretical capability will have cross-cutting impacts beyond specific systems, with the potential to deliver breakthrough science. The techniques and codes we will develop are very general and applicable to many other problems, for example strongly correlated transition metal oxides and materials with lanthanide and actinide elements. By establishing highly accurate benchmark calculations, the results will validate less computer intensive methods. The capability of these tools will allow a new level of prediction and understanding of nano-structured materials.

FY 2014 HIGHLIGHTS

Frozen orbital and downfolding method with auxiliary-field quantum Monte Carlo (AFQMC): We demonstrated an approach that can provide great computational savings, downfolding high-energy basis states to a physically relevant low-energy sector, which allows a systematic approach to produce realistic many-body model Hamiltonians. As a by-product, we obtain a way to effectively eliminate the error due to single-projector, norm-conserving pseudopotentials in AFQMC. [Wirawan Purwanto *et al.*, *Journal of Chemical Theory and Computation*, 2014 DOI: 10.1021/ct4006486.]

Stability, Energetics, and Magnetic States of Cobalt Adatoms on Graphene: We investigate the stability and electronic properties of single Co atoms on graphene with near-exact many-body calculations. A frozen-orbital embedding scheme was combined with auxiliary-field quantum Monte Carlo calculations to increase the reach in system sizes. Several energy minima are found as a function of the distance h between Co and graphene. The findings provide an explanation for recent experimental results with Co on free-standing graphene. [Yudistira Virgus *et al.*, *Phys. Rev. Lett.*, 2014, DOI: 10.1103/PhysRevLett.113.175502. (Paper Received 2 July 2014; published 23 October 2014).]

Quantum Monte Carlo calculations in solids with downfolded Hamiltonians: We applied the downfolding approach to extended systems. Many-body calculations operate on a simpler Hamiltonian which retains material-specific properties. The Hamiltonian is systematically improvable and allows one to dial, in principle, between the simplest model and the original Hamiltonian. [Submitted to *Phys. Rev. Lett.* Dec 2014.]

Theoretical Modeling of Spin-Forbidden Channels in Combustion Reactions

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Funding: \$125,000 (2014)

PROGRAM SCOPE

The goal of our research is to develop predictive theoretical methods, which can provide crucial quantitative data (e.g., rate constants, branching ratios, heats of formation), identify new channels and refine reaction mechanisms. Specifically, we are developing tools for computational studies of spin-forbidden and non-adiabatic pathways of reactions relevant to combustion, and applying these tools to study electronic structure and reactions of open-shell and electronically excited species involved in these processes.

FY 2014 HIGHLIGHTS

During the past year, we conducted several computational studies of open-shell and electronically excited species. The common theme in these studies is interactions between states of different character and intersections between the corresponding potential energy surfaces. We also continued to develop and benchmark computational methods for modeling electronic structure and spectroscopy of open-shell species. Particular emphasis was placed on determining spectroscopic signatures of transient species, to facilitate comparisons with experimental data. In 2014-2015, the DOE support has been acknowledged in six papers. Two more papers are being prepared for the publication. The highlights include investigations of conical intersections, developing protocols for calculating redox properties and energetics of hydrate transfer reactions, developing an validating codes for Dyson orbitals and cross section calculations (including condensed phase), as well as developing formalism and codes for efficient calculations of spin-orbit couplings.

Computational Design of Metal Organic Frameworks for Photocatalytic Reduction of Carbon-Dioxide

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Funding: \$269,832 (2014-2015)

PROGRAM SCOPE

The utilization of light as a direct means of energy production and as an aid to catalyze chemical reactions are examples of key technological applications depending on the interaction of light with matter. There is an urgent need to understand light-matter interactions to determine fundamental processes in photoactive materials with an ultimate goal of optimizing materials for various applications. Developments of new simulation methodologies are required to contribute abundantly to the discovery and innovation process in partnership with advances in synthesis and characterization. In this project, our research team will continue to develop advanced methods to examine excitation dynamics and light-matter interactions in materials. More specifically, as outlined in the project narrative, we will utilize computational tools in a high-throughput search for porous coordinated polymers that

incorporate organic linkers that undergo photo-isomerization, that is, conformation changes as a result of light irradiation; azobenzene is a well-studied example of a molecule with photo-isomerization properties. Porous coordinated polymers (PCPs) that utilize stimuli response, such as light absorption, are shown to be potentially highly efficient sorbents, particularly for carbon dioxide uptake.

FY 2014 HIGHLIGHTS

More recently, we have been investigating the photo-isomerization processes in azo-functional organic linkers through non-adiabatic molecular dynamics. We are exploring the impact of R-groups on the optical properties, isomerization reaction time, and quantum yield and we find that these properties are strongly dependent on the functional groups attached to the azobenzene derivative. We will report on non-adiabatic molecular dynamics simulation results for a few model azobenzene derivative systems and we will discuss our theoretical understanding of the trans- to cis- transformation mechanisms, and timescale variations, resulting from different functional groups. Our long term goal is to use high-throughput calculations to rationally design highly efficient photo-isomerization response in porous coordinated polymers for gas separation. Two publications regarding this research have been accepted and are currently in print.

Time-Dependent Density Functional Theory: Introducing First-Principles Electron Friction in Time-Domain

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Funding: \$90,000 (2014)

PROGRAM SCOPE

Excited state multi-electron dynamics is fundamental to describing the electronic behavior of molecules in photochemical reactions, dynamics at metal or semiconductor surfaces, and electron transfer in molecular, biological, interfacial, or electrochemical systems. Providing accurate and experimentally meaningful descriptions of excited state electronic dynamics within the real-time time-dependent density functional theory (RT-TDDFT) framework has been the focus of our research during this funding period. Our research supported by this DOE award has been focusing on extending the capability of RT-TDDFT electronic dynamics to probe excited state dynamics in response to external perturbations such as solvent and molecular vibrations. In a real physical/chemical system, multi-electron wave function decoherence arises from bath-induced fluctuations in the system. From the perspective of electrons, the bath can be the collective solvent degrees of freedom or the molecular vibrations. Within the framework of first-principles electronic dynamics, we have developed several different techniques to address the electronic decoherence arising from interactions with solvent and molecular vibrations. New methods include a real-time, time-dependent polarizable continuum model (RT-TDPCM) method to model electron-solvent interactions with an open-system framework, a first-principles friction/dissipation formalism to model thermalized electronic equilibration processes, and a concept of mixed quantum/classical molecular dynamics that combines surface-hopping and an excited Ehrenfest potential to model electron-phonon coupling.

FY 2014 HIGHLIGHTS

In this funding period (Oct13 - Sept 14), we have published four peer-reviewed papers. Highlights of our recent work of RT-TDDFT electronic dynamics funded by this DOE award include: A plasmon-like phenomenon, arising from coinciding resonant excitations of different electronic characteristics in 1D silver nanowires, has been proposed based on theoretical linear absorption spectra. Such a molecular plasmon holds the potential for anisotropic nanoplasmonic applications. However, its dynamical nature remains unexplored. Recently, we have carried out the real-time time-dependent density functional theory to study the quantum dynamics of longitudinal and transverse excitations in 1D silver nanowires. The anisotropic electron dynamics confirm that the transverse transitions of different electronic characteristics are collective in nature and oscillate in-phase with respect to each other. Analysis of the time evolutions of participating one-electron wave functions suggest that the transverse transitions form a coherent wave packet that gives rise to a strong plasmon resonance at the molecular level. "In-Chain Donor/Acceptor block copolymers" comprised of alternating electron rich/poor moieties are emerging as promising semiconducting chromophores for use in organic photovoltaic devices, but a mechanistic understanding of the relevant charge diffusion pathways is lacking. To elucidate the mechanisms of electron and hole transport following excitation to optically accessible low-lying valence states, we utilize RT-TDDFT to explicitly track the evolution of these photo-accessible states. From the orbital pathway traversed in the dynamics, p and n type conductivity can be distinguished. The electronic dynamics for the studied polymers show the time-resolved transitions between the initial photoexcited state, a tightly-bound excitonic state that is dark to the ground state, and a partially charge separated state indicated by long-lived, out-of-phase charge oscillations

Hydration Mechanisms in Nanoparticle Interaction and Surface Energetics

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Funding: \$127,196 (2014)

PROGRAM SCOPE

Emerging nanoparticle technologies require new techniques to control surface properties of a material. In many applications, surface thermodynamics and interactions between nanoparticle surfaces are determined by solvation in electrolyte solutions. The long-term objective of this research is to develop molecular level understanding of energetics, kinetics and hydration in nanoparticle solutions, and ionic solutions in particular. The program focuses on modulating surface free energy and hydration effects in prototypical nanoscale systems through surface functionalization or applied electric field in the presence of conducting (ionic) solution. A further goal concerns molecular mechanisms and the intricate role of salt in surface energy storage in a nanoporous medium controlled by an externally applied electric field. The project relies on a combination of theoretical and computational approaches using atomistic and coarse-grained models to span different length and time scales. The efforts involve development of optimized algorithms for molecular simulations of nanoscale surface phenomena, focusing on the interplay of applied and ion-induced electric field and hydrogen bond interactions. Theoretical studies of the new effects this project is uncovering will likely inspire future experiments. Understanding of basic molecular mechanisms involved in solvation of nanoparticles represents an important step in creating

new materials, harvesting energy from nature and storing energy. In nanotechnology, this understanding is essential for effective control of surface interactions and nanocolloid phase behavior. It also underlies the development of novel separation techniques in ionic systems, exemplified by water desalination and soil decontamination.

FY 2014 HIGHLIGHTS

Salt partitioning and phase behavior of electrolytes in porous media can be efficiently modulated by ionic patterning and by applying electric field. Our molecular modeling studies reveal new and unexpected features in both the fast and slow responses of aqueous and solution interfaces to electric stimuli. Specifically, we uncover a strong and nonmonotonic polarity dependence of reorientation dynamics at aqueous interfaces. Order of magnitude acceleration can be achieved in a narrow window of applied field strengths provided the field is pointing toward the solid phase. We developed new computational algorithms for multiphase electrolyte system to capture the slow response, which involves transport of salt and solvent under the influence of the field. Using a novel, self-consistent formulation of the heterogeneous field problem, we show an unambiguous contraction of the solution relative to surrounding bath. This resolves an open literature debate on the role of the external field and provides a route to studies of the electrolyte influence on static and dynamic partitioning of solution components. Of particular importance for materials and energy technologies, we identified a range of conditions where electrolyte solution manifests revertible permeation/expulsion transitions, allowing material flow and storage of surface energy subject to voltage regulation. Nanoscale porosity is mandated for successful operation. We quantify the extent of salt depletion and concomitant weakening of the substrate/solution adhesion. The counterbalancing effect of the rise in solution surface tension stabilizes the permeated state, an outcome of immense importance because of ubiquitous materials exposure to saline solutions.

Electron-Ion Dynamics with Time-Dependent Density Functional Theory: Towards Predictive Solar Cell Modeling

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Funding: \$86,249 (2014)

PROGRAM SCOPE

The overall goal is to develop accurate and reliable practical methods to model dynamical processes in solar cells, and eventually be used in their design. Purely electronic aspects of the problem (electronic dynamics and excitations), as well as the coupling of the electron motion to the nuclear motion, need improvement over their present-day treatments. From the electronic side, the usual approximations in time-dependent density functional theory (TDDFT) perform poorly for charge-transfer processes, and little is known about how the adiabatic approximations used perform when simulations begin after the initial photo-excitation (in theory they are not supposed to be applied here). Studying exactly-solvable model systems enables us to find features of the exact exchange-correlation potential that are essential for accurate dynamics, and compare with approximations. In particular for real-time dynamics, such as involved in a transfer of a photo-excited electron from a donor to acceptor, one must go beyond the

linear response regime, and it is unclear whether approximations known to be accurate for excitation spectra perform well. Turning to the problem of coupling with ions, more needs to be understood about the reliability of using TDDFT in conjunction with surface-hopping, yet Ehrenfest provides an inadequate description of the coupling. Originally I had proposed a method coupling semiclassical nuclei to TDDFT electrons, and, in working towards this, exploring different aspects of the exact factorization approach to coupled electron-ion dynamics, in collaboration with the Halle group. This approach has a rigorous foundation, and is the correct starting point for approximations. The potentials of the theory contain new terms that exactly account for electron-ion coupling, and we are studying their main features for non-adiabatic dynamics in the absence and presence of external fields, comparing them to the potentials used in surface-hopping and Ehrenfest.

FY 2014 HIGHLIGHTS

We showed that propagating with the adiabatically-exact functional (i.e. the best possible adiabatic approximation) fails to transfer charge across a long-range molecule, despite capturing nonlocal ground-state step features relevant to dissociation and often accurately capturing charge-transfer (CT) excitations. The dynamics is highly non-perturbative, and calls for functionals beyond the ones developed for excitations. A second result is a new exact condition we proved that has particular implications for time-resolved spectroscopy. A fundamental property of a system driven by an external field is that when the field is turned off, the response frequencies are independent of the time at which the field is turned off. The Kohn-Sham potential typically continues to evolve, leading to time-dependent Kohn-Sham response frequencies. The exchange-correlation kernel must cancel out this time-dependence, yielding an exact condition based on generalized response theory. The condition is typically violated, but we showed a simple functional on a 2-electron model of photo-excited CT satisfies the condition, and consequently fully CTs accurately. Regarding coupled electron-ion dynamics, with collaborators from MPI Halle, we found that quasiclassical propagation of an ensemble of nuclear trajectories on the exact time-dependent potential energy surface is extremely accurate in describing branching of a nuclear wavepacket in a model non-adiabatic CT problem. Further, we related features of the exact surface to aspects of surface-hopping, like velocity renormalization. We see hints of a force-induced decoherence, but more care is needed to fully analyze this aspect. We used the exact factorization to define the exact potential acting on the electronic system, and compared this to traditional potentials used to study laser-induced electron localization, a technique developed for attosecond control of electrons. Important differences found give different localization asymmetries.

Ultrafast Processes in Atoms and Molecules: Integrated Treatment of Electronic and Nuclear Motion in Ultrashort XUV Pulses

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Funding: Research was supported with prior fiscal year funding. (2014)

PROGRAM SCOPE

This project addresses the physics of new kinds of short laser pulse spectroscopy for studying the dynamics of electrons in atoms and molecules. We are developing and applying a new theoretical and

computational method for describing the response of atoms and diatomic molecules to intense ultrashort pulses of electromagnetic radiation. The project has refined and extended a new computational implementation of the Multiconfiguration Time-Dependent Hartree Fock (MCTDHF) approach to solving the time-dependent Schrödinger equation in which all electrons are treated dynamically on the same footing. This computer code is being used to predict and study the dynamics of population transfer between electronic excited states of molecules in femtosecond pulses of ionizing radiation and to the interpretation of transient absorption and multidimensional spectra of atoms and diatomic molecules.

FY 2014 HIGHLIGHTS

This year our efforts have focused on applications and development of the Multiconfiguration Time-Dependent Hartree Fock (MCTDHF) method in three areas:

- 1) Population transfer between valence states using autoionizing states as intermediates. Our work on this subject appeared this year in Physical Review A, and it demonstrates the remarkable result that roughly 40% of the population of the ground state of the NO molecule can be transferred within 1 femtosecond to a wave packet of valence states through autoionizing states 400 eV above the ground state.
- 2) MCTDHF applications to attosecond transient absorption in the ionization continuum of atoms and molecules: An attosecond transient absorption experiment is one in which a time delayed, intense near infrared (NIR) pulse is used to modify the absorption of a weaker, attosecond UV pulse that came before it or overlapped with it. We have discovered that there exists a way to use this idea to probe the electron dynamics driven by the intense NIR pulse in intensity regimes where it generates high harmonics. This could be a new way to investigate the intense field dynamics that are responsible for high harmonic generation in molecules.
- 3) The development of a new capability for using MCTDHF in a non-perturbative approach to XUV multidimensional spectroscopy, including 3 and 4 wave mixing: We implemented a way to apply the macroscopic phase matching condition that determines the final signal in a multidimensional spectroscopy experiment with several short pulses. During this phase of the project we have made a discovery that these ideas can be applied to transient absorption, and that experiments with two pulses, an IR and an XUV pulse, that have the pulses propagating in different directions could be used to decompose transient absorption spectra into contributions of different numbers of IR photons.

Theoretical Studies of Chemical Reactions Related to the Formation and Growth of Polycyclic Aromatic Hydrocarbons and Molecular Properties of Their Key Intermediates

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Funding: \$220,000 (2014-2015)

PROGRAM SCOPE

We investigate complex chemical mechanisms of PAH formation and growth via theoretical studies of their critical elementary reactions. Our primary objectives include (i) to unravel reaction mechanisms

through detailed, accurate, and reliable calculations of pertinent potential energy surfaces (PESs); (ii) to compute rate constants for individual reaction steps and total absolute reaction rate constants and product branching ratios depending on reaction conditions, such as collision energy or temperature and pressure; (iii) to characterize molecular, energetic, and spectroscopic parameters of various possible reaction intermediates and products including their enthalpies of formation, geometric structure, vibrational frequencies and rotational constants, as well as photoionization and photoexcitation spectra. To achieve these goals, we employ chemically accurate *ab initio* and density functional calculations (using CCSD(T)/CBS, G3, and explicitly correlated methods) of the PESs of these reactions which are then utilized for statistical (TST and RRKM/Master Equation) computations of absolute reaction rate constants and product branching ratios. In the current project period we study the reactions of dicarbon C_2 with unsaturated hydrocarbons producing resonance-stabilized free radicals (RSFR), which in turn can contribute to the formation of aromatic species, the isomer-specific growth of various PAH and CP-PAH molecules beyond the second aromatic ring, and the oxidation of PAH radicals. The studies of the reactions of the p-tolyl radical with isoprene, 1,2-butadiene, and C_3H_4 isomers, and the reaction of the phenyl radical with isoprene leading to the formation of methyl-substituted PAH molecules indene and naphthalene are performed in conjunction with crossed molecular beams experiments in Kaiser's group. Another collaborative project is underway with Arthur Suite's group on the studies of Cl atoms with alkenes occurring via a Cl-addition-radical-roaming mechanism.

FY 2014 HIGHLIGHTS

We elucidated the chemical dynamics of the formation of toluene through a single collision event of the ethynyl radical C_2H and isoprene in the gas phase. The reaction has no entrance barrier, is exoergic, and all transition states are located below the energy of the separated reactants and hence can lead to toluene not only in high-temperature combustion flames, but also in low-temperature environments. The substitution of the methyl group at the C_2 carbon atom of isoprene by any alkyl group might lead to the synthesis of alkyl-substituted benzene molecules. This reaction class presents a facile alternative to the formation of alkyl benzenes through reactions of benzene with alkyl radicals underscoring the importance of ethynyl-radical-mediated formation of aromatic molecules in combustion flames from acyclic precursors through barrierless and strongly exoergic reactions from noncyclic precursor molecules. Similarly, we discovered that the reaction of triplet dicarbon with isoprene forms the aromatic and resonantly stabilized free radical benzyl providing a barrierless pathway via a single collision event from acyclic, non-aromatic reactants. The reaction of triplet C_2 with isoprene may form benzyl both in combustion flames and in low temperature astrochemical environments. We performed VRC-TST/RRKM-ME calculations of total rate coefficients and product branching ratios for the oxidation of phenyl and naphthyl radicals with O_2 at temperatures relevant to combustion (1500, 2000, and 2500 K) and pressures of 0.01, 0.1, 1.0, and 10 atm. The results gave the rate coefficients in the range of $3.0\text{--}5.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ with slightly positive temperature dependence. The dominant reaction channel is elimination of the O atom from peroxy complexes leading to the phenoxy and naphthoxy radical products. Chemically-activated phenoxy and naphthoxy radicals either decompose to the cyclopentadienyl+CO and indenyl+CO products, respectively, or undergo thermal equilibration.

Testing the Applicability and Potential Impact of Rigorous Quantum Embedding Methods for the Study and Characterization of Metal Organic Frameworks

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Funding: Research was supported with prior fiscal year funding. (2014)

PROGRAM SCOPE

The PI develops theoretical and computational methods to understand a variety of molecular processes, including enzyme catalysis, solar energy conversion, dendrite formation in lithium batteries, and the dynamics of soft matter and biological systems. An important aspect of this challenge is that many systems exhibit dynamics that require a means for embedded density functional theory. This research develops new techniques that can bridge dynamical hierarchies and simulate complex dynamics.

FY 2014 HIGHLIGHTS

A paper reporting accurate and systematically improvable density functional theory embedding for correlated wavefunctions is accepted to the journal of Physical Chemistry. A paper on embedded mean-field theory was accepted for publication in JCTC. The PI won the ACS Physical Division Early-Career Award in Theoretical Chemistry.

Manipulating Light with Transition Metal Clusters, Organic Dyes, and Metal-Organic Frameworks

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Funding: \$180,000 (2014-2015)

PROGRAM SCOPE

The primary goals of our research program are to develop and apply state-of-the-art first principles methods to predict electronic and optical properties of three systems of significant scientific and technological interest: Transition metal clusters, organic dyes, and metal-organic frameworks. These systems offer great opportunities to manipulate light for a wide ranging list of energy-related scientific problems and applications. We focus our investigations on the following areas:

- The development and implementation of many-body Green's function methods (solving the GW-Bethe-Salpeter Equation) to examine excited state properties of transition metal clusters.
- The prediction of optical properties of free-standing and dye-sensitized titania nanocrystals. For free-standing nanocrystals, we examine the size, shape, and exposed surface dependence of the optical properties of passivated TiO₂ nanocrystals and investigate whether or not the bulk-limit can be achieved with a reasonably sized nanocrystal amenable to a first-principles treatment. We will also consider the perylene-diimide based organic dyes on various TiO₂ surfaces to investigate how the optical properties of the combined system emerge from its individual units.
- The pioneering applications of time-dependent density functional theory and many-body perturbation methods to examine the electronic and optical properties of metal-organic frameworks to shed light on whether they can be utilized as materials for light-harvesting applications. In particular, we will focus on two metal-organic frameworks, the so-called MOF 5 and HKUST-1, and their building units, and perform a systematic study of how their optical properties evolve from their

subunits. These studies are expected to lead to significant insights for future design of alternative photovoltaic and photocatalytic materials based on metal organic frameworks.

FY 2014 HIGHLIGHTS

We have modeled rutile TiO₂ nanocrystals (NCs) up to ~1.5 nm in size to study the effects of quantum confinement on their electronic and optical properties. Electronic excitations were obtained via the perturbative GW approximation and Delta-SCF method for NCs up to 24 and 64 TiO₂ formula units, respectively. These demanding GW computations were made feasible by our implementation of a real-space framework that exploits quantum confinement to reduce the number of empty states needed in GW summations. We used TDDFT to predict the optical properties of NCs up to 64 TiO₂ units. Our computations revealed that the largest NCs modeled are still quantum confined and do not yet have quasiparticle levels or optical gaps at bulk values. Nevertheless, we found that classical Mie-Gans theory can quite accurately reproduce the line shape of TDDFT absorption spectra, even for TiO₂ NCs of subnanometer size. We have started a new collaboration with two groups (Chelikowsky at UT Austin and Louie at UC Berkeley) to benchmark a variety of molecules to determine any trends in the accuracy of GW+BSE computations relative to experiment, particularly in reference to (i) the impact of a LDA-derived vertex correction compared to the standard GW calculations without vertex corrections, and (ii) the effect of self-consistency in GW. The set so far includes three inorganic molecules (N₂, H₂O, and NH₃) and six organic molecules (benzene, naphthalene, thiophene, 1,2,5-thiadiazole, benzothiazole and tetrathiafulvalene). Preliminary results were presented at the 2014 APS March meeting in Denver, CO. We have started a new collaboration with the group of Leor Kronik (Weizmann Institute, Israel) on investigating the electronic structure of copper-oxide clusters (Cu_xO_y, x=1-2, y=1-4) using optimally-tuned range-separated hybrid functionals as well as the GW method at various levels of theory. Preliminary results will be presented at the 2015 APS Meeting, San Antonio TX.

Theoretical Studies of Spin Crossover Metal-Organic Frameworks

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Funding: \$180,000 (2014-2015)

PROGRAM SCOPE

The main goal of our research project is to characterize the physical mechanisms that determine the spin crossover (SCO) behavior of metal-organic frameworks (MOFs). MOFs represent a relatively new class of porous materials consisting of metal ions coordinated to organic ligands. In most cases, the pores are stable to elimination of solvent molecules, which results in open spaces of high surface area suitable for gas storage and purification, separation processes, and heterogeneous catalysis. The presence of transition metal centers with unpaired electrons, such as Fe(II) and Co(II), can also add magnetic properties to the framework. This provides new opportunities for the design of multifunctional MOFs with SCO behavior in which changes in the electronic structure of the metal centers lead to distinctive changes in the overall geometry, color, and magnetism of the material. Although the SCO behavior has been observed in several MOFs, its connection to the physicochemical properties of the framework, the nature of the guest molecules, and the ligand field of the metal centers remain poorly

understood. Our studies aim at providing a molecular-level understanding of the physical mechanisms that affect the SCO behavior of MOFs through the development and application of new theoretical/computational approaches. The specific objectives are:

- Development of a novel computational methodology, which encodes electronic structure data into a molecular mechanics description of the frameworks for simulating both electronic and structural properties of MOFs with SCO behavior.
- Molecular-level understanding of the effects of the framework properties, such as ligands functionality and flexibility, on the SCO behavior of MOFs.
- Identification of the molecular interactions that determine the adsorption of chemically different guest molecules and, consequently, modulate the SCO behavior of MOFs.

FY 2014 HIGHLIGHTS

We have developed a novel hybrid Monte Carlo / molecular dynamics (MC/MD) method that builds upon the ligand field molecular mechanics (LFMM) approach and enables modeling of SCO properties in bulk materials, including MOFs. Within LFMM, conventional molecular mechanics (MM) energy expressions are supplemented with an additional term that effectively represents the ligand field stabilization energy (LFSE) arising from the splitting and different occupation of the d orbitals of the metal centers. LFMM thus explicitly includes energy contributions that depend on both the instantaneous coordination geometry and the electronic structure of the metal centers. To enable direct simulations of the SCO properties of MOF materials, we have improved upon the original LFMM approach and combined it with a Monte Carlo scheme based on the Metropolis acceptance/rejection criterion that is used to model the transitions between different spin states. We then extended our hybrid MC/MD scheme to systems with multiple metal centers in periodic boundary conditions. Our MC/MD approach, implemented in a modified version of the publicly-available DL_POLY Classic software, is thus designed to describe generic SCO materials with an arbitrary number of different metal centers, each with its own set of possible spin states. We carried out hybrid MC/MD simulations for the $[\text{Fe}(\text{pz})_2\text{Pt}(\text{CN})_4]$ MOF, which displays bidirectional chemo-switching of spin states upon adsorption of different guest molecules. The magnetization curve of the SCOF material obtained with our hybrid MC/MD correctly reproduces the sharp transition between the low-spin and high-spin states observed experimentally (Inorg. Chem 2014, 53, 11020). To the best of our knowledge, our hybrid MC/MD method is the first approach that enables direct simulation of spin crossover in bulk materials, effectively capturing electronic-driven processes within a physically-based computational scheme.

Interactions, Phase Equilibria and Self-Assembly in Ionic Systems

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Funding: \$150,000 (2014)

PROGRAM SCOPE

Work under this project focuses on studies of activity and osmotic coefficients in salt solutions using atomistic models, self-assembly of ionic surfactants, and analysis of structure, thermodynamics and dynamics of ionomer membranes. For calculations of free energies of salt solutions, we use

thermodynamic integration and staged insertions. Atomistic models that can be used in a fully predictive mode offer distinct advantages over previously available phenomenological and implicit-solvent models; their performance at elevated temperatures, which are important for separation and CO₂ geophysical sequestration applications, has not been previously determined. In the area of polymer electrolyte membranes, which are used in fuel cell applications, the main focus is on the effects of water content on the internal structure, dynamics, permeability, and mechanical properties of the membranes. Finally, in the area of ionic surfactant self-assembly, we are investigating the effects of added salt on the cmc, aggregation number, and aggregate morphology, the effects of temperature, the dynamics of surfactant exchange between micelles and free solution and of micelle breakup and reformation, and the relationship between grand canonical Monte Carlo methods for determining critical micellar concentrations and the methods based on extrapolation with respect to total surfactant loading.

FY 2014 HIGHLIGHTS

Two key components of our work on polymer electrolyte membranes were completed in FY 2014 and have appeared as publications in the Journal of Physical Chemistry. In the first paper (vol. 118, pp 8798-8807, 2014), atomistic molecular dynamics simulations were reported over a wide range of water contents and temperatures to obtain a better understanding of the structural and transport aspects of water sorption in a widely used polymer electrolyte, Nafion. In the second paper (vol. 118, pp. 13981-91, 2014), the mechanical stiffness and structure of Nafion were studied in the limit of a low water volume fraction using molecular dynamics simulations. The viscosity was shown to increase by up to 4 orders of magnitude in response to changes in composition representing as little as 2 wt % of system, specifically with respect to changes in the counterion type. In the area of phase behavior of aqueous electrolytes, simulations have been carried out to obtain thermodynamic and transport properties of the binary mixture H₂O + NaCl at temperatures from T = 298 to 473 K [J. Chem. Phys., 141: 234507 (2014)]. Vapor pressures, liquid densities, viscosities, and vapor-liquid interfacial tensions have been obtained as functions of pressure and salt concentration. Several previously proposed fixed-point-charge models that include either Lennard-Jones 12-6 or exponential-6 functional forms to describe non-Coulombic interactions were studied. While none of the model combinations are able to reproduce simultaneously all target properties, optimal model combinations for specific properties were identified.

A Theoretical Investigation of the Structure and Reactivity of the Molecular Constituents of Oil Sand and Oil Shale

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

Our work focuses on the theoretical characterization of the gas phase structures, energies and reactivities of the molecular constituents of asphaltenes contained in oil sand and oil shale. Asphaltenes represent an untapped source of hydrocarbon fuel in North America; however, information about the molecular nature of these deposits has only recently become available and very little is known about the reaction pathways, combustion efficiency and reactivity of these species. We are currently

characterizing the combustion and pyrolysis reaction channels available to asphaltene constituents such as thiophene and methyl thiophene. Initially, we are using DFT to perform conformational surface scans of the reaction space for each system. Once viable reaction channels have been identified, these are further characterized using higher level, explicitly correlated methods.

FY 2014 HIGHLIGHTS

We have been pursuing 3 lines of investigation related to our DOE-funded goal of better understanding radical reactions through theoretical investigation. We have focused our efforts on: 1) characterizing the pyrolysis and combustion pathways of small model compounds of asphaltenes; 2) learning to use properly highly correlated, multi-reference methods such as the Spin-Flip (SF), Multi-reference Averaged-Quadratic Coupled Cluster (MR-AQCC) and Mukherjee Multi-reference Coupled Cluster (Mk-MRCC) methods for describing the multi-configurational character, energies and structures of diradicals; 3) Applying these methods to the characterization of unusual radical species and/or reactions.

Spin-Forbidden Chemical Reactions in Catalysis from First-Principles

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PROGRAM SCOPE

When multiple spin states cross in the reaction pathway, spin-orbit interaction allows for non-adiabatic hopping between the spin surfaces and hence leads to spin transfer between reactant and products, making possible reactions that otherwise would be spin-forbidden. The goal of the proposed research is to develop computational tools for the first-principles modeling of these type of reactions, with particular emphasis on catalytic reactions with transition metals and heavy elements. We will employ noncollinear spin density functional theory to optimize the local atomic spin magnetization direction and the nuclear coordinates along the reaction path, including spin-orbit interaction. To this end, we will implement algorithms based on a constrained minimization to search for noncollinear spin states that are expected to emerge close to the spin-crossover region, as well as in transition metal clusters present in the reaction as catalysts. Spin-orbit interaction will be fully included in the search of the reaction path using the all-electron Douglas-Kroll-Hess approximation or, optionally, relativistic effective core potentials. The outcome of the proposed research will enhance our understanding of the basic processes involved in chemical reactions, and lead us to apply our methodology to several practical problems. One of particular interest is the study of nanometer-sized transition metal clusters as non-conventional catalysts for hydrocarbons, a topic that has drawn a lot of attention lately due to its implications for energy and in the chemical industry.

FY 2014 HIGHLIGHTS

Papers published:

- The Performance of Density Functional Approximations for the Structures and Relative Energies of Minimum Energy Crossing Points, B. A. Abate and J. E. Peralta Chem. Phys. Lett. 590, 227-230. (2013).

- Magnetic Exchange Couplings from Noncollinear Perturbation Theory: Dinuclear CuII Complexes, J. J. Phillips and J. E. Peralta J. Phys. Chem. A asap (2014).
- Site-specific Polarizabilities from Analytic Linear-response Theory, J. E. Peralta, V. Barone, and K. A. Jackson Chem. Phys. Lett. 608, 24-27 (2014).

New Single-and Multi-Reference Coupled-Cluster Methods for High Accuracy Calculations of Ground and Excited States

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 Funding: \$144,000 (2014)

PROGRAM SCOPE

This research program focuses on new generations of *ab initio* electronic structure methods and computer codes exploiting the single- and multi-reference coupled-cluster (CC) wave function ansätze, which can provide an accurate description of chemical reaction pathways, molecular electronic excitations, challenging cases of electronic near-degeneracies, and properties other than energy. The goal is to design and apply affordable approaches that enable precise modeling of molecular processes and properties relevant to combustion, catalysis, and photochemistry. The emphasis is on development of methods that offer high accuracy, ease of use, and lower computational costs compared to other approaches that aim at similar precision, so that one can study complex molecular problems with dozens or hundreds of atoms, in addition to smaller systems, in a predictive manner. Among the most successful methods developed to date are the completely renormalized (CR) CC and equation-of-motion CC (EOMCC) approaches, the local, low-order-scaling, CC methods for larger polyatomic systems, and the active-space CC/EOMCC approaches. Substantial progress in genuine multi-reference CC theories has been made as well. The CR-CC methods and their open-shell, local, and excited-state generalizations extend the conventional single-reference theories to multi-reference situations created by radicals, biradicals, bond breaking, and two-electron excitations with an ease of a black-box computation. The active-space CC and EOMCC approaches, their electron-attached and ionized extensions, and the genuine multi-reference CC methods enable practical high-accuracy calculations for a wide variety of closed-shell, open-shell, and strongly correlated electronic states. The most promising approaches developed in this program are shared at no cost with the community through the GAMESS package. Some of the best methods discovered in this program are also available in NWChem.

FY 2014 HIGHLIGHTS

We developed and tested the doubly electron-attached and doubly ionized EOMCC theories with full and active-space treatments of high-order 4-particle-2-hole (4p2h) and 4-hole-2-particle (4h2p) excitations, which are applicable to open-shell species with two electrons outside the closed-shell cores, particularly to electronic spectra of biradicals, without invoking more complex steps of genuine multi-reference CC theories. The resulting DEA- and DIP-EOMCC methods with an active-space treatment of 4p2h and 4h2p excitations reproduce the results of the analogous full calculations at the tiny fraction of the computer effort, while allowing one to determine the singlet-triplet and singlet-singlet gaps in biradicals to within fractions of kcal/mol. We also demonstrated that the DEA- and DIP-EOMCC

approaches with up to 4p2h and 4h2p excitations provide results that are almost insensitive to the choice of the underlying molecular orbital basis, which should be contrasted with the analogous methods truncated at 3p1h/3h1p excitations that are less accurate and sensitive to the orbital choice. As a follow-up of our successful FY13 work on structural, electronic, and catalytic properties of gold nanoparticles using CC methods and codes developed by our group, we used our IP-EOMCC approaches correlating valence and semi-core electrons, accounting for scalar relativistic effects, and including up to 3h2p terms to investigate the photoelectron spectrum of the negatively charged gold trimer, providing an accurate assignment of peaks and shoulders in the experimental photoelectron spectrum for the first time. We also computed potential energy surface (PES) cuts of the ground and several singlet and triplet excited states corresponding to the dissociation of water into the OH and H fragments and demonstrated that our black-box, single-reference CR-CC and CR-EOMCC methods produce PESs that are competitive with those obtained with the expert high-level multi-reference CC approaches.

Investigation of Non-Premixed Turbulent Combustion

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Funding: \$153,428 (2014)

PROGRAM SCOPE

LES/PDF approaches are now well developed, and can be applied to turbulent combustion problems involving complex flows with strong turbulence-chemistry interactions. However, the computational cost is quite high, thus limiting the approach to simple fuels with relatively small chemical models. The objective of this project is to develop and validate an adaptive chemistry approach for use in LES/particle PDF methods. The adaptive strategy allows for individual particles to evolve according to a reduced set of kinetic equations tailored for their specific compositions, thereby significantly reducing both the time and memory required for a computation with a given kinetic mechanism, and enabling affordable computations with significantly more detailed chemistry descriptions. Rather than performing chemical reduction at runtime to determine the optimal set of equations to use for a given particle, a time consuming task limiting the benefits of the adaptive approach, an *a priori* analysis of the composition space region likely accessed during the turbulent flow simulation is performed using simple Partially Stirred Reactor computations. Our approach relies on an *a priori* partitioning of the composition space into a user-specified number of regions, over which suitable reduced chemical representations and chemical models are identified automatically. A computational particle in the LES/PDF simulation evolves according to, and carries only the variables present in the reduced representation corresponding to the composition space region it belongs to. This region is identified using a low-dimensional binary tree search algorithm, thereby keeping the run-time overhead associated with the adaptive approach to a minimum. The methodology is coupled with RCCE dimension-reduction techniques and ISAT. The final objective of this project is to demonstrate the computational benefits of this approach in a large-scale LES/PDF simulation of a turbulent jet flame with detailed chemistry.

FY 2014 HIGHLIGHTS

In FY 2014, the research has focused on the following two topics: the development and optimization of the methodology to implement adaptive chemistry in particle PDF simulations; and the coupling of the adaptive chemistry framework with a previously developed RCCE-based dimension-reduction methodology. Major accomplishments include an improved Directed Relation Graph with Error Propagation (DRGEP) algorithm that simultaneously eliminates non-important species and reactions, an extension of the DRGEP concept for kinetic analysis and characterization, a rigorous mathematical formalism to partition the composition space into regions with markedly distinct chemical characteristics, and a fully automatic implementation of the proposed adaptive methodology, which will greatly facilitate the integration with any Computational Fluid Dynamics Simulation software. The methodology has been tested in Partially Stirred Reactor (PaSR) configurations burning a non-premixed mixture of propane and air. Results indicate that for a similar overall computational cost, using a set of reduced models adaptively using the proposed strategy increases accuracy by one to two orders of magnitude compared to a conventional non-adaptive approach, that is, using a single reduced chemical model valid over the entire composition space. Preliminary results also show that combining DRGEP and RCCE reduction methodology may decrease the memory requirements by an additional factor of two. The adaptive chemistry methodology and results have been reported in a manuscript to be submitted to Combustion and Flame. In addition, the improved DRGEP methodology has been used in two additional research articles so far.

Exploring the Random Phase Approximation for Materials Chemistry and Physics

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PROGRAM SCOPE

The project addresses the applicability of the many-body random phase approximation (RPA) for materials science. The RPA has the ability to capture effects beyond standard density functional theory (DFT) approximations. The correlation energy of the RPA is long-ranged, thus it captures van der Waals interactions. RPA also has the exact exchange energy as an ingredient, therefore it is suitable for some dissociation problems, barrier heights and adsorption challenges in condensed matter physics. Despite these attractive features, RPA suffers some shortcomings in its correlation part. These deficiencies can be potentially corrected by 'beyond-RPA' approximations, i.e.; nonlocal kernels or energy corrections. These corrections can boost the accuracy of the RPA for several materials problems, like the dissociation of the H^{2+} molecular ion, the structural phase transition of SiO_2 , and possibly the adsorption of CO on the silver surface. The RPA is related to GW, a many-body approximation which targets band gap calculations. The application or implementation of GW is usually not straightforward in materials science; it is applied mostly in a perturbative way (G_0W_0). Even if there are recently attempts for a consistent input for perturbative GW, the broad applicability of these methods is limited. In the project we want to estimate the effect of the input potential for certain solids and molecules, especially targeting strongly-correlated materials. A potential uniform and computationally affordable input is also the aim.

FY 2014 HIGHLIGHTS

In the past year, my research group was focusing on structural phase transitions with RPA. We have produced two papers in this area (PRB). One of them gives an estimation of the RPA on the structural phase transition in Si crystals. The other work targeted the structural phase transition in strongly correlated VO₂. In this case the sub-projects 'structural phase transitions' also have an overlap with another part of the projects; the 'strongly-correlated materials'. Relying on these results we are working on an implementation of a nonlocal uniform-electron-gas based kernel to RPA. This kernel is currently being implemented in the ABINIT electronic structure code. Tests will be performed at first on the cohesive energies of semiconductors, where the RPA shows significant deficiencies from its correlation contribution. The PI published recently a work in JCTC about the systems with anion- π interactions. This work gives a detailed assessment of RPA and related methods for weak interactions in molecules. Parallel to this work, the PI is working on a benchmark test for 'beyond-RPA' methods on reaction test sets from organic chemistry. This work is close to be submitted. The PI is also working to assess different inputs for perturbative GW on transition metal monoxides.

Surface Plasmon Enhanced Chemistry

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Funding:	\$380,000 (2014-2015)

PROGRAM SCOPE

This project is concerned with the development of computational methods and new theory that enables one to describe plasmon excitation in metal nanoparticles, and the interaction of plasmon excited states with molecules and semiconductor nanoparticles that are nearby the metal nanoparticles. Plasmon excitation leads to dramatic modification to the optical and chemical properties of molecules or nanoparticles that are located near the surfaces of these particles, in some cases leading to enhancement in chemical reactivity or optical properties such as extinction, absorption, and Raman (SERS). Also of interest are theories of time-resolved processes such as transient absorption, and the evolution of initial electronic excitation into phonons and solvent. The research program seeks to develop new electronic structure theories that can be coupled to continuum theories such as Maxwell's equations to describe the interaction of light with plasmonic metal particles leading to plasmonically enhanced chemistry and enhanced spectroscopic properties. In addition, the methods being developed will be used to model experiments being done by a number of collaborators.

FY 2014 HIGHLIGHTS

A new theory for describing plasmon enhanced optical properties was developed which combined a previously developed DFT approach for calculating the chemical contribution to the enhancement factor with a coupled QM/electrodynamics calculation. This is the most complete theory developed so far for SERS. We also performed further studies of our real-time TDDFT approach to photoinduced electron transfer, and we summarized past work on plasmonically enhanced dye-sensitized solar cells. We collaborated with experimental groups to characterize plasmons for dimers of silver particles that are

separated by less than 1 nm. Also, we characterized plasmons for many rod segments that are pieced together with small gaps, and we studied plasmons in spherical structures that consist of a dielectric core and a shell of small gold nanoparticles that acts as a continuous shell. In theory work, we discovered that the plasmon width for Al is dominated by radiative effects, which is fundamentally different from that for Ag and Au, providing new opportunities for Al. We demonstrated how the optical properties of arrays of particles can be modified by both the nanoscale properties of the particles and the mesoscale properties of the array. And we develop a theory of refraction at metal-metal interfaces. We discovered plasmon enhanced lasers that combine lattice plasmons in combination with laser dyes to enhance stimulated emission. We also performed detailed studies of the transient absorption behavior of semiconducting nanoparticles that has led to new understanding of thermal flow from electronic excitation to phonons to solvent, including for quantum confinement effects.

Enabling Technologies for High-Throughput Screening of Nano-Porous Materials: Collaboration with the Nanoporous Materials Genome Center

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Funding: Research was supported with prior fiscal year funding. (2014)

PROGRAM SCOPE

The objective of this research program is to develop and apply the theoretical framework necessary to generate transferable “physically-motivated” classical force fields for complex systems, with an emphasis on nano-porous materials for gas separation applications. The overarching goal is to develop models which include, by construction, the right balance of all of the relevant “physics” of intermolecular interactions, with the physical properties of interest emerging as a natural consequence. We make use of symmetry-adapted perturbation theory calculations, exploiting the resultant energy decomposition to parameterize force fields which enforce the right balance of exchange, electrostatics, polarization, and dispersion, thus generating robust and transferable force fields that yield the right answer, for the right reason. We find that the resulting force fields exhibit tremendous transferability, allowing simulation of essentially arbitrary compositions (mixtures, heterogeneous systems, etc.) without re-parameterization. This transferability is not coincidental, but, within the context of the approach, arises naturally from the universality of the underlying physical laws governing intermolecular interactions. We have applied this basic methodology to a variety of complex systems, but with a particular emphasis on the development of transferable force fields for nano-porous metal-organic framework (MOF) materials. We have extended the approach outlined above to generate physically-motivated force fields for adsorbate-MOF interactions and a comprehensive “library” of functional group and metal parameters that covers a sizable fraction of all known (or potentially synthesizable) MOFs. More recently, emphasizing the generality of this approach, we showed that the methodology can also generate accurate and transferable models for a wide range of systems ranging from gases, to bulk organics, to strongly interacting ionic liquids.

FY 2014 HIGHLIGHTS

A significant output of our work over the past several years is a “library” of accurate and transferable force field parameters for MOFs, which can be utilized to screen MOFs for their gas adsorption and separation properties using computational approaches. Recently, in collaboration with Randy Snurr (Northwestern), we examined the sensitivity of such high-throughput screenings with respect to the quality of the force field, contrasting our force fields with simpler “standard” models (which have not been optimized for MOFs). Interestingly, we find that although quantitative results may differ substantially (by 100%!), the correlation between predictions accurate and “standard” models is strong, thus suggesting that pre-screening with efficient standard force fields is a feasible strategy. Significantly, we also established the generality of our force field development methodology well beyond MOFs. We showed that, by including appropriate three-body dispersion interactions, our “physically motivated” methodology yields accurate results even for bulk liquids even in absence of empirical refinement. We also showed that we can even extend the approach to strongly interacting ionic liquids (ILs). Here, we developed, for the first time, an entirely first-principles based model for the prototypical [BMIM][BF₄] system which yields essentially quantitative accuracy with a wide range of physical properties. Currently, we are working to extend our approach to systems which interact non-perturbatively (e.g. adsorption on MOFs with open metal sites) using variational energy decomposition methods. We are also working to generalize our methodology to account for highly anisotropic interactions (e.g. lone pairs, hydrogen bonding systems), using a simple, and computationally efficient formalism. These advances will further increase the accuracy and transferability of our approach, while largely maintain compatibility with standard simulation packages.

Accurate Excited States via Symmetry Projected Approaches

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Funding: \$138,779 (2014)

PROGRAM SCOPE

While electronically excited states are of primary importance in many energy-related processes, their theoretical description is quite challenging. Accurate ground state methods cannot generally be used to describe excited states because they cannot enforce the condition that the ground and excited states be orthogonal. Our recently developed projected quasiparticle theory (PQT) and the closely related projected Hartree-Fock theory (PHF), however, have particularly simple structures which makes enforcing this orthogonality condition feasible. In this project we have extended PQT and PHF to the study of excited states, even those with the same spatial and spin symmetries as the ground state. We are planning to apply our techniques to important problems as spin-spin interactions in molecular magnets, singlet-triplet splittings, and photon absorption and energy conversion in dendrimers.

FY 2014 HIGHLIGHTS

This is the second year of this grant. During 2014, there were 8 publications acknowledging support to this grant. We are very happy with the progress achieved in this project. Briefly, the most salient bullets

are: (1) The calculation of excited states for the one-dimensional Hubbard model with different quantum numbers (spin, space group) which can be compared to exact results; (2) The calculation of singlet-triplet energy splittings with projected Hartree-Fock on challenging cases; (3) The development of a multi-component symmetry projected approach; and (4) the evaluation of excited states on extremely difficult proof-of-principle systems like C_2 .

Electronic Structure Theories of Singlet Fission and Multiple Exciton Generation

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Funding: Research was supported with prior fiscal year funding. (2014)

PROGRAM SCOPE

The objective of this project is to develop novel multireference electronic structure theory to understand the mechanism of the singlet fission processes in solar energy conversion. Singlet fission is a molecular analogue of multiple exciton generation, in which a single photon is converted to two charge carriers. Since the final state is a two-exciton state, standard time-dependent density functional theories cannot be applied, which warrants theory development. In this project, we develop a new theory based on the so-called active space decomposition ansatz, and obtain mechanistic insights into the processes. This research would help rationally design such materials. In addition, developed programs will be interfaced to an open-source BAGEL package, which is publicly available to end users.

FY 2014 HIGHLIGHTS

We have developed a method, in which large active space wave functions are decomposed into a linear combination of products of fragment active space wave functions. Our method is not only a clever way of performing active space computation of unprecedented size, which is necessary for accurate description of excitonic processes, but also a novel way to map chemical systems to tensor networks that have been developed in condensed matter physics. The extensions of the ASD method to restricted active space (RAS) wave functions were performed in this research. In addition, we have established a methodology with which we construct accurate few-state diabatic model Hamiltonians from our ASD method. The model Hamiltonians are the basis of dynamics simulations using a quantum-master-equation formalism. We have implemented the method into an efficient, parallel program that scales well at least up to 512 CPU cores. The program has been openly distributed in the BAGEL package. The above methods have been applied to singlet fission processes in pentacene and tetracene crystals to derive the diabatic model Hamiltonians. We have demonstrated that the coupling between the initial states and charge-transfer intermediate states are strong (~ 100 meV), and that the direct coupling between the initial and final two-exciton states is less than 1 meV in both cases, supporting a mechanism mediated by the charge-transfer states. We have also validated the use of diabatic states in the mechanistic studies of singlet fission.

Plasmon Enhanced Photovoltaics: Modeling Energy and Charge Transfer in Solar Nanoassemblies

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Funding: Research was supported with prior fiscal year funding. (2014)

PROGRAM SCOPE

The overarching goal of the project is to better understand how energy and charge move through assemblies of nanomaterials such as wide bandgap semiconductors, strongly absorbing dye molecules, and plasmonic nanoparticles. The former two are highly relevant for current photovoltaic devices and the latter are known to have unique optical properties resulting from surface plasmon excitations. We want to determine if the highly tunable plasmon modes supported by the metal particle – and the sizeable electromagnetic fields generated upon exciting them – can be utilized to enhance the chemical and physical processes associated with photovoltaic devices. Energy and charge transfer in multicomponent nanoassemblies are being investigated using a variety of modeling and simulation techniques, including classical electrodynamics, density functional theory, and ab-initio molecular dynamics. We are also developing a hybrid method that describes both the electromagnetic and chemical processes that occur when molecules are in close proximity to metal surfaces.

FY 2014 HIGHLIGHTS

We have demonstrated that plasmonic components can efficiently direct incident electromagnetic energy into thin semiconductor layers. Light absorption in a plasmonic grating nanosurface can be calculated by means of a simple, analytical model based on a transmission line equivalent circuit. We have shown the utility of the circuit theory for understanding how the peaks in the absorption coefficient are related to the resonances of the equivalent transmission model and how this can help in designing more efficient structures. We have also investigated a two-dimensional corrugated plasmonic nanosurface for robust light trapping. The two-dimensional configuration is more efficient than its one-dimensional counterpart in terms of the short circuit photocurrent density. We have extended these studies to treat the interactions between a molecule and a metal nanoparticle. We find that the molecular absorption and emission processes are drastically altered by the presence of a metal nanoparticle and the degree of inter-nanoparticle coupling. The latter is important because plasmon fields become extremely large in nanoparticle junctions. When a molecule is placed within the gap of a strongly coupled nanoparticle dimer, the radiative decay rate is enhanced notably more than the non-radiative channels for the dimer compared to the single nanoparticle. The result is a suppression of quenching in the dimer case until the molecule is in very close proximity to the metal surface (~2 nm); single nanoparticles quench the emission readily for a metal/molecule distance inside of 15 nm.

Quantum Chemistry of Radicals and Reactive Intermediates

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PROGRAM SCOPE

My research group works in the area of theoretical chemical physics, especially on the thermodynamic properties, spectra, and reactions of organic radicals and other transient intermediates. In addition, we are active developers of software for both computational electronic structure and what might be termed computational spectroscopy. Our quantum chemistry research follows a number of paths, including first-principles calculations of bond energies and other thermochemical information (as well as development of methodology for such calculations), methods for the simulation and analysis of molecular spectroscopy, especially those relevant to experiments that can be used to glean thermochemical information, and the development of *ab initio* methods needed for the accurate treatment of transient organic molecules.

FY 2014 HIGHLIGHTS

- We have carried out a kinetic analysis of the ozonolysis reaction that will soon be submitted for publication.
- We have implemented a very efficient version of the so-called CCSDTQ and CCSDT(Q) methods.
- We have made a systematic study of basis set effects on the harmonic frequencies and transition mode frequency for transition states.

Variational Transition State Theory

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Funding: \$143,000 (2014)

PROGRAM SCOPE

This project involves the development of variational transition state theory (VTST) including optimized multidimensional tunneling (OMT) contributions and the application of this theory to gas-phase reactions with a special emphasis on developing reaction rate theory in directions that are important for applications to combustion. The further development of VTST/OMT as a useful tool for combustion kinetics also involves (i) developing and applying new methods of electronic structure calculations for the input potential energy surface, which is typically an implicit surface ("direct dynamics") defined by a level of electronic structure theory, (ii) methods to interface reaction-path and reaction-swath dynamics calculations with electronic structure theory, and (iii) methods to treat vibrational anharmonicity and vibration-rotation coupling. The project also involves the development and implementation of practical techniques and software for applying the theory to various classes of reactions and transition states and applications to specific reactions, with special emphasis on combustion reactions and reactions that provide good test cases for methods needed to study combustion reactions. The direct dynamics approach to gas-phase reactions in this project involves electronic structure calculations of potential energy surfaces and the use of these surfaces to calculate generalized free energies of activation and multidimensional tunneling probabilities. A key emphasis is the interface of electronic structure calculations with dynamics algorithms as achieved in the POLYRATE computer program and its various RATE interfaces to electronic structure packages.

FY 2014 HIGHLIGHTS

We made progress in the several areas, including: (i) the development of a method for adding tunneling to classical trajectory calculations, (ii) the development of a new method for obtaining reactive force fields from electronic structure calculations, (iii) the prediction of experimentally unavailable product branching ratios for biofuel combustion, and (iv) the development of an improved method for Feynman path integral calculations of anharmonic partition functions, free energies, enthalpies, entropies, and heat capacities. Next I single out one of these areas for a more detailed summary: Isobutanol is a prototype biofuel, and sorting out the mechanism of its combustion is an important objective where theoretical modeling can provide information that is unavailable and not easily obtained by experiment. In the work we carried out, the rate constants and branching ratios for the hydrogen abstraction reactions from isobutanol by hydroxyl radical were calculated using multi-path variational transition-state theory with small-curvature tunneling. We used hybrid degeneracy-corrected vibrational perturbation theory to show that it is critical to consider the anharmonicity difference of high-frequency modes between reactants and transition states. We showed that to obtain accurate rate constants, we must apply different scaling factors to the calculated harmonic vibrational frequencies at the reactants and at the transition states. The factors determining the reaction rate constants have been analyzed in detail, including variational effects, tunneling contributions, the effect of multiple reaction paths on transmission coefficients, and anharmonicities of low- and high-frequency vibrational modes. The analysis quantified the uncertainties in the rate calculations. A key result of the work is a prediction for the site dependence of hydrogen abstraction from isobutanol by hydroxyl radical.

Quantum Chemistry via Walks in Determinant Space

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Funding:	Research was supported with prior fiscal year funding. (2014)

PROGRAM SCOPE

The main purpose of this Collaborative Research Team (CRT) is to improve upon the recently developed initiator full-configuration interaction quantum Monte Carlo (i-FCIQMC) method, with the goal of developing a highly accurate method for treating difficult chemical systems of interest to the DOE. Another goal is to have cross-fertilization of ideas between i-FCIQMC and phaseless Auxiliary Field quantum Monte Carlo (AFQMC), developed by the Zhang-Krakauer group, since both methods employ walks in a space of determinants.

FY 2014 HIGHLIGHTS

We have implemented non-abelian symmetries for the Hubbard model in our recently developed semistochastic quantum Monte Carlo (SQMC). Inclusion of the symmetries greatly reduces the size of the walker population needed and thereby the efficiency of the method. We have demonstrated the efficacy of using projected Hartree-Fock (PHF) wave functions as the trial wave function in constrained path Monte Carlo calculations. The PHF approach gives a hierarchy of wavefunctions of increasing quality -- the more symmetries that are broken and restored in a self-consistent variation-after-

projection approach the higher the quality of the wavefunction. In tests on the 2-D Hubbard model, the PHF wave functions gave highly accurate results (as benchmarked by constraint-release). One of the key advantages of the PHF wave functions is that their computational cost, unlike a multiconfiguration self-consistent field (MCSCF) wave function, scales polynomially with system size. In collaboration with Garnet Chan's group at Princeton, George Booth at Cambridge, and Takeshi Yanai in Japan we have implemented an F12 method to enhance the convergence of energies and other properties to the infinite basis limit.

Theoretical Studies of the Reactions, and the Spectroscopy of Radical Species Relevant to Combustion Reactions and Diagnostics

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Funding: \$160,000 (2014)

PROGRAM SCOPE

My research deals with nonadiabatic chemistry a ubiquitous area of chemical physics in which molecular motion transitions radiationlessly between coupled potential energy surfaces thereby interconverting distinct forms of chemical energy. Nonadiabatic processes may be initiated by the absorption of a photon and consequently are relevant to vision, photosynthesis, solar energy storage and combustion relevant processes including nonadiabatic electron detachment and photoionization, and molecular photodissociation, with the later two processes being the focus of our DoE funded research. A principal goal of our research, is to bring state of the art electronic structure methods to bare on nonadiabatic dynamics simulations. Currently the preponderance of nonadiabatic reactive dynamics is carried out using on-the-fly or direct dynamics, in which the electronic structure data is determined as required by a call to the electronic structure program. While easy to implement and use, this approach suffers from two limitations (i) the determination of the electronic structure data is slow so to obtain reasonable turnaround times low-level (low accuracy) electronic structure methods are used, and (ii) the electronic structure data suffers from discontinuities as a result of the requisite changes in the active space as distinct channels are explored. Our fit coupled surfaces approach avoids these issues. It is based on high-level (high accuracy) multireference configuration interaction single and double excitation wave functions and it is least squares based so it has the ability to smooth out the discontinuities in the electronic structure data. Since the electronic structure data is represented by a diabatic Hamiltonian H_d whose blocks are described by polynomial forms, the time to determine the electronic structure data at a single point is on the order of tens of milliseconds, compared to minutes or even hours in direct dynamics. The challenge is to construct H_d .

FY 2014 HIGHLIGHTS

In our DoE funded research we have focused on applications of the fitting algorithm. Our recent construction of an H_d for the multichannel, multistate, nonadiabatic photodissociation of hydroxymethyl, studied experimentally by Reisler (USC), has demonstrated the potential of this approach. A manuscript is being prepared, which describes the representation, in the full nine dimensional internal coordinates, of 3 potential energy surfaces coupled by conical intersections and

producing 3 distinct dissociation channels, $\text{CH}_2\text{O}+\text{H}$, cis- and trans- $\text{HCOH}+\text{H}$. This high quality representation which is based on 67 million configuration state functions (CSFs), and made possible by a grant of computer time from NERSC, is unique in this field. A second paper describing the use of this Hd to simulate the production of the dominant $\text{CH}_2\text{O} +\text{H}$ channel is also being prepared. In this later study a statistically significant simulation is achieved using 10,000 surface hopping trajectories for each laser energy. Using on-the-fly techniques only ~ 100 such trajectories, using much less sophisticated wave functions, would be possible. In a second tour de force calculation we are constructing an Hd to describe the photodissociation of phenol, $\text{C}_6\text{H}_5\text{OH}+\text{h}\nu \rightarrow \text{C}_6\text{H}_5\text{O}+\text{H}$, from its excited S_1 and S_2 states. This work which is nearing completion, uses 4 diabatic states, based on ~ 100 million CSFs, and is performed in the full 33 dimensional internal coordinate space. It too is made possible by a grant of computer time from NERSC. As part of an ongoing study of the spectra of cyclo-alkoxy radicals, which complements the experimental work of Miller(OSU) we have reported a study of the ground state of cyclopentoxy. We have shown that, contrary to all previous calculations, the ground electronic state is correctly described as the component of a two state pseudo Jahn-Teller system.

EARLY CAREER: Accurate *Ab-initio* Methods for Correlated Surface Problems

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Funding: \$150,000 (2014)

PROGRAM SCOPE

Transition metal surfaces are widely used in heterogeneous catalysis; however, modeling of catalytic processes on such surfaces remains very challenging due to the difficulty in describing accurately the electronic correlation in the d-orbitals of the transition metals for bulk problems containing thousands of atoms. The objective of this project is to develop new theoretical techniques to address the challenge of correlated surfaces and to properly describe different correlations present between the localized, strongly correlated d-orbitals and the delocalized, weakly correlated s- and p-orbitals in a systematically improvable, ab-initio manner. In this project, methods from both condensed matter physics and quantum chemistry will be employed to build a computationally feasible embedding approach that tackles the size of the problem. This newly developed approach will be used to study the complex interactions between molecule and surface, to model directly measurable experimental quantities such as the photoelectron spectra and to enable a systematic search for new classes of catalytic materials.

FY 2014 HIGHLIGHTS

We have developed three new methods during the first year of support.

1. Iterative GF2 (Green's function second order) scheme (J. Chem. Phys. 140, 241101 (2014))
2. A method for parametrizing model Hamiltonians used in Green's function's method (J. Chem. Phys. 141, 194105 (2014))
3. Self-energy embedding method that is the one of the most efficient schemes for combining GF2 and the self-energy coming from ED method (arXiv:1410.5118, Phys. Rev. B to be published)

The PI has given 8 talks acknowledging DOE support.

Two supported graduate students won poster awards (Yao Li Physical Chemistry Division in Indianapolis, 2013, Alexei Kananenka during Midwestern Meeting of Theoretical Chemistry, Northwestern 2014).

Density Functional Based Software for the X-ray Based Spectra

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PROGRAM SCOPE

The X-ray based core-hole spectroscopy (XPS, XAS (EXAFS and NEXAFS), XES) are important techniques in materials characterization. Through X-ray induced hole creation and decay process, a variety of information about the system such as the chemical state, nature of chemical bonding, local geometric structure etc. can be obtained using these techniques. The project concerns development of a suite of software at various levels of sophistication to perform calculations of core-hole excitation spectra using the first principles methods such as density functional theory. This includes development of robust suite of Perl/Python scripts to perform calculations on core-hole excitations of large systems on computers with large number of processors in parallel. Another software development component is Graphical user interface development for visualization, for setting up the inputs for calculations using pull up and pop-up menus, and for execution and analysis of calculated spectra. The GUI development is aimed at bringing the core-hole calculations to the level of use-friendliness so that it could also be used for classroom teaching of core-hole spectroscopy and molecular physics. Apart from software development, recently developed perturbative delta SCF method for charge transfer excitations will be adapted and further refined for the core-hole excitation. A few other developments such as implementation of simple self-interaction schemes for core-electron binding energies will be implemented and tested.

FY 2014 HIGHLIGHTS

The following developments were carried out: i) The GUI development was extended to allow plotting of generated spectra and molecular orbitals, ii) a number of widely used Gaussian basis sets were included so that users can now specify the name of the basis set, iii) the part of the code which calculates the intensities of transition is parallelized. The parallelization of the code that calculates intensities was tested on a light harvesting β -Carotene-Porphyrin- C_{60} triad, which due to its large size, creates a bottle neck in the serial calculation of joint density of states, as originally only the master node performed required calculation of transition dipoles. This test was at our university's research cloud using 84 processors. We obtained reduction in time from 12,721 to 956 secs. The scaling tests were also performed subsequently and the code was found to scale fairly well up to 300 processors. The GUI allows plotting of calculated spectra. A tutorial screencast of how to use GUI for setting up calculations and post processing the outputs is made available in YouTube. As performance test of the overall development of the code, we have studied the dielectric properties of endohedral fullerenes and carbon onions. The site specific partitioning of polarizabilities indicates that the polarizability of the endohedral fullerene is essentially due to the outer fullerene cage and has insignificant contribution from the encapsulated unit. Thus outer fullerene cages effectively shield the encapsulated clusters and behave like Faraday cages. The application of the site specific polarizabilities to $C_{60}@C_{240}$ and $C_{60}@C_{180}$ onions

shows that the encapsulation of C_{60} in C_{240} and C_{180} fullerenes reduces its polarizability by 75% and 83%, respectively. The differences in the polarizability of C_{60} in two onions are a result of differences in the bonding (intershell electron transfer), fullerene shell relaxations, and intershell separations.

DOE National Laboratories

Chemical Physics - Base Program

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Funding: \$485,000 (2014)

PROGRAM SCOPE

The primary focus of the theoretical Chemical Physics program at Ames Laboratory is the development and extensive application of methods that enable the study of condensed-phase and surface reaction phenomena, especially heterogeneous catalysis. The program supports an integrated effort including both electronic structure theory and non-equilibrium statistical mechanical and multiscale modeling. Also of interest are solvent effects, mechanisms of homogeneous catalysis in organometallic chemistry, and excited states in large molecular systems. Electronic structure theory efforts combine development of fundamental theory, expanding the capability for accurate treatment of large systems of interest to U.S. Department of Energy, Basic Energy Sciences, with optimal strategies for computational implementation within GAMESS. Theory development includes fragment molecular orbital and effective fragment potential approaches with applications to liquid-solid interfaces, and embedding methods for solid surfaces. A newer focus is on excited states and non-adiabatic dynamics with applications to photocatalysis. Statistical mechanical and multiscale modeling studies focus on catalytic reaction-diffusion phenomena often incorporating input from electronic structure analyses. A core focus is the predictive molecular-level modeling of chemisorption and heterogeneous catalysis on metal surfaces, including fundamental studies of catalytic poisoning transitions. We also implement heterogeneous multiscale modeling for spatiotemporal behavior on extended surfaces, and analyze fluctuation-mediated behavior in nanoscale catalyst systems. Other major efforts include modeling of the interplay between restricted transport and catalytic reaction in functionalized mesoporous materials, and modeling of reaction processes on non-conducting surfaces. There are extensive collaborations with the Ames Laboratory program "Homogeneous and Interfacial Catalysis in 3D Controlled Environments".

FY 2014 HIGHLIGHTS

We detailed the inhibited molecular passing processes in narrow pores; the passing propensity strongly impacts reaction yield for catalytically functionalized nanoporous materials. We modeled the effects of multifunctionalization of these materials to enhance reaction yield. We developed a general, but realistic and predictive molecular-level stochastic model for CO-oxidation on metal(100) surfaces for Pd, Rh, Pt, and Ir. Density functional theory and Kinetic Monte Carlo simulations led to insight into local-environment dependence of the sticking probability for dissociative adsorption of oxygen on metal(100)

surfaces, noting that this process is a critical step in catalytic oxidation reactions. With the catalysis program, a new mixed oxazoline-carbene borate Zn compound was found to provide isolable monomeric Zn alkylperoxide. We showed that there is a significant distortion of the Zn methyl group from the pseudo tetrahedral position as a result of subtle electronic rather than steric effects. Full, highly accurate potential energy curves were calculated for the 4 lowest lying singlet states of the CEEIS method for electron correlation recovery. Excellent agreement was found with all known vibrational-rotational spectral data and dissociation energies. A quantitative analysis of H^{2+} , H_2 , B_2 , C_2 , N_2 , O_2 , F_2 has shown that the intra-atomic contraction of atomic valence shells occurs because it enhances the inter-atomic delocalization and, thereby, lowers the kinetic energy. This result confirms that covalent bonds are created by the drive of electron waves to lower their kinetic energy by expansion. The dynamics package NEWTON-X and the occupation restricted multiple active space method in GAMESS were interfaced for nonadiabatic and adiabatic on-the-fly dynamics simulations. Single excitations between the orbital subspaces qualitatively recovered the state populations. Orbital integrity issues were shown to be more prevalent than previously thought.

Theoretical and Computational Tools for Modeling of Energy Relevant Catalysis on Multiple Scales

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PROGRAM SCOPE

This theory and computation program develops new strategies for and integrated combinations of electronic structure analysis and statistical mechanical, coarse-grained, and multi-scale modeling approaches to treat energy-relevant heterogeneous catalytic systems. Currently, there is a lack of effective molecular-level modeling for overall catalytic reaction processes and a critical need to incorporate high-level energetics for predictivity. Essential to these efforts is development of novel new approaches in not only theoretical chemistry and materials science (BES), but also computational science and applied mathematics (ASCR). Applications motivating the work include analysis of catalysis in mesoporous oxides and catalysis on metal and oxide surfaces.

FY 2014 HIGHLIGHTS

We have developed an efficient Kinetic Monte Carlo simulation algorithm for general, realistic molecular-level multi-site stochastic lattice-gas modeling of catalytic CO-oxidation on unreconstructed metal(100) surfaces. In addition, we established analytic theories to describe: (i) multi-stability as well as bistability in CO-oxidation kinetics; (ii) nucleation-mediated CO-poisoning kinetics, i.e., nucleation of "droplets" the CO-poisoned-phase embedded in a metastable reactive phase. We also have developed an analytic statistical mechanical description of the local-environment dependence of the sticking probability for dissociative adsorption of oxygen on metal(100) surfaces. We implemented strongly-damped Langevin dynamics (including rotational diffusion), and also adaptive-mesh finite-element-method analysis of the equivalent Fokker-Planck equations, describing of inhibited molecular passing processes in narrow pores; the associated passing propensity strongly impacts reaction yield for catalytically functionalized nanoporous materials. We have developed the theory for the fully analytic

gradient for density functional theory (DFT) based on the fragment molecular orbital (FMO) method. This is very important for future applications of FMO/DFT to heterogeneous catalysis. Furthermore, we have demonstrated the theory for the combination of nonlinear spectroscopic techniques with the EFP method to study the effects of solvent on nonlinear optics.

Simulating the Generation, Evolution and Fate of Electronic Excitations in Molecular and Nanoscale Materials with First Principles Methods

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Funding: \$756,000 (2014)

PROGRAM SCOPE

There are strong existing limitations on calculations of bound excited states in large molecules, and for resonance states in any polyatomic molecule. These limitations partly reflect deficiencies of existing software and algorithms. But more fundamentally they also reflect limitations of existing methods and models, particularly for resonances, or where multiple electrons are excited, or strong electron correlations are in play. The overall goal of this proposal is to make meaningful progress by coupling new and improved models for bound and metastable excited states from physical scientists with advances on underlying methodological challenges in applied mathematics, and practical realization via high performance computing. This will be achieved by developing new and reduced scaling methods for bound excited states in large molecules, and adapting modern electronic structure methods to treat resonance states using a rigorous approach based on complex scaling. Object-oriented tensor libraries will be used to implement these methods, and as a platform for introducing compact decompositions to increase efficiency. Linear algebra developments center on the eigensolvers needed for excited states, and a strong coupling to leadership class computing is built into the work plan.

FY 2014 HIGHLIGHTS

For strongly correlated bound states, the formulation of spin-flipping methods was improved in two significant ways. First, second order perturbative corrections were developed that replace variational evaluation of excitations external to the active space with large speedups. Second, a novel variational spin-flip procedure that uses configuration-specific non-orthogonal orbitals to remove the need for external excitations was developed. For unbound states, the first implementation of the method of complex basis functions into a modern electronic structure program was achieved (for the static exchange model), and demonstrated on polyatomic molecules of up to a dozen atoms. Progress was made in the formulation and implementation of a fully grid-based Hartree-Fock program. To treat the tensors that arise in electronic structure theory, a variety of developments in a tensor library were

completed. These developments increase numerical performance, give demonstrably improved parallel scaling on shared memory architectures, and lay the ground for more effectively using distributed memory massively parallel computing resources. Improvements in solvers for the non-Hermitian complex eigenvalue problem, which is central to treating resonances by the complex basis function method, were also achieved.

Theoretical/Computational Studies of the Fundamentals of One Component and Alloy Based Nanocatalysis Relevant to Alternative Sources of Energy

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Funding: \$169,000 (2014)

PROGRAM SCOPE

This project constitutes a program of theoretical/computational studies that aim at advancing our fundamental understanding of one-component and alloy metal based nanocatalysis relevant to alternative sources of energy. The emphasis is on unraveling and characterizing the separate and combined roles of the structural and electronic features of metal nanocatalysts and the key mechanisms that underlie their activity and selectivity. These are investigated as a function of the catalyst particles size and composition, both elemental and percentile. Among the primary targets are catalysts and reactions for efficient conversion of hydrocarbons into alternative sources of energy. The main computational tools here are those of density functional theory. The work is carried out in close contact with the related experimental work at Argonne and elsewhere. Our emphasis is on fundamental scientific issues, which in addition to those mentioned above also include the important in the context of catalysis aspect of thermal stability and thermally induced structural and phase transformations of alloy nanoparticles. This aspect of the studies involves methodological developments and is carried out using molecular dynamics techniques in combination with semiempirical potentials.

FY 2014 HIGHLIGHTS

We performed detailed computational studies of catalytic reforming reactions of glycerol, $C_3O_3H_8$, and its derivatives, which are relevant to conversion of biomass into liquid fuels and other chemicals. As a prototypical case, we considered the $C_3O_3H_7$ derivative, which is a precursor of hydroxyacetone, $C_3O_2H_6$, identified as the most abundant intermediate in initial stages of glycerol reforming. We obtained and characterized the various possible adsorption conformations of 8 forms of $C_3O_3H_7$ on pure Pt_7 and mixed Pt_5Mo_2 and Pt_3Mo_4 nanocatalysts. The two energetically most preferred adsorption complexes for each nanocatalyst were then used as reactant states, and for each reactant the full minimum energy paths for all possible abstractions of an H atom, an OH group, or an O atom, as appropriate, were mapped out. For each path, the barrier height and the reaction exothermicity were quantified and the reaction mechanism was characterized. We have found that multiple paths can be energetically competitive and that some reactions that involve O-H bond scission in $C_3O_3H_7$ proceed via an accompanying H transfer within the molecule. Analysis of the nanocatalyst composition effects on activity and selectivity revealed that the presence of Mo leads to reduction in barrier heights for the dehydrogenation and dehydroxylation reactions. This reduction is larger for dehydroxylation, and for both reactions the

degree of reduction increases with the Mo concentration. Other aspects of the performed studies include exploration and characterization of the interactions of H₂, both molecular and dissociative, with Pd_n, n=2-4, 7 and 13, nanocatalysts as a function of the catalyst size and the degree of hydrogen coverage up to and including the saturation limit (relevant for direct synthesis of H₂O₂ from H₂ and O₂), and application of a new dynamical descriptor – the time-dependent mixing coefficient - for a refined analysis of temperature-induced structural changes in alloy nanoparticles.

An Expert *Ab Initio* Transition-State-Theory-Based Master Equation Code

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Funding: \$147,000 (2014)

PROGRAM SCOPE

The goal of this project is to develop expert codes for accurately predicting the kinetics of gas phase chemical reactions. The *ab initio* transition state theory based master equation (AITSTME) approach provides the basic framework for this effort. The code development effort is designed to facilitate all aspects of the implementation of the AITSTME approach while also increasing its utility through further advances in its theoretical underpinnings. A successful code package will be widely used in the modeling of key reactions in combustion chemistry, atmospheric chemistry, astrophysics, and chemical vapor deposition, for example.

FY 2014 HIGHLIGHTS

Our new general-purpose AITSTME software package, which is termed PAPER (Predictive Automated Phenomenological Elementary Rates), implements a new formulation of the master equation for complex-forming chemical reactions with multiple wells and multiple bimolecular products. The PAPER code, which is now finding widespread use within our team and in external research efforts, incorporates a variety of advances beyond other existing codes, including automated merging of species as their equilibration rates exceed collisional stabilization rates, threaded parallelization of the key diagonalization step, and a procedure for properly modeling the separation into thermal and direct kinetics for hot initial distributions. These advances allow for improved accuracy in the predictions while also greatly reducing the effort involved in making the predictions. In exploratory work, we have developed a method for making accurate *a priori* predictions of the pressure dependence of the kinetics. This work required the solution of a two-dimensional master equation (2DME) in energy E and angular momentum J, as well as accurate calculations of collision induced E and J transfer rates. New methods for characterizing details of the collisional transfer function that are not typically considered (J-dependence, E/J coupling, etc.) were developed and implemented in the molecular dynamics code DiNT, while a new two-dimensional master equation code was developed. In other work, DiNT was further improved with a new method for predicting spin-forbidden kinetics and with options for computing exact classical diffusion coefficients. A particularly useful approximation for estimating Lennard Jones

parameters was interfaced with our universal PESs and incorporated into a stand-alone code called OneDMin.

Next Generation First Principles Molecular Dynamics

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PROGRAM SCOPE

Molecular dynamics (MD) simulation is one of the most general and widely used methods for obtaining a broad variety of properties in computational chemistry, materials science and molecular biology, such as phase transitions, molecular structures, and chemical reactions. Most MD simulations depend on a parametrization of a simplified classical model of the atomic interaction potential. These simulations are often not very reliable because of limited transferability between the unknown systems of interest and the original set of parameterized structures. First principles MD derived from self-consistent field (SCF) theory such as density functional theory (DFT) offers a more rigorous and reliable alternative. DFT based MD simulations within the Born-Oppenheimer (BO) approximation of uncoupled electronic and nuclear motion is regarded as one of the most reliable standards for atomistic simulations. Unfortunately, first principles BOMD is often limited by some fundamental shortcomings, such as a very high computational cost or unbalanced phase-space trajectories, numerical instabilities and a systematic long-term energy drift. These problems are often either accepted as an unavoidable limitation or simply ignored, for example, by using thermostats that cover up an unphysical underlying dynamics. The overreaching goal of this proposal is to go beyond conventional BOMD and create a framework for a new generation of first principles MD schemes that overcome previous shortcomings and limitations. This will open the door to reliable and highly efficient atomistic simulations of large complex systems that radically extends current capabilities.

FY 2014 HIGHLIGHTS

- 1) "Extended Lagrangian Born-Oppenheimer molecular dynamics in the limit of vanishing self-consistent field optimization", P. Souvatzis and A.M.N. Niklasson, *J. Chem. Phys.* 139, 214102 (2013)
- 2) "First principles molecular dynamics without self-consistent field optimization", P. Souvatzis and A.M.N. Niklasson, *J. Chem. Phys.* 140, 044117 (2014)
- 3) "Generalized extended Lagrangian Born-Oppenheimer molecular dynamics", A.M.N. Niklasson and M.J. Cawkwell, *J. Chem. Phys.* 141, 164123 (2014).

The first two publications presents the first demonstrations of first principles based extended Lagrangian BOMD using a single diagonalization and Hamiltonian construction per time step, yielding trajectories that are practically indistinguishable from "exact" BOMD. The demonstrations of these fast "0-SCF" simulations were performed at the theory level of Hartree-Fock (1) and DFT including hybrid functionals (2). This new capability allows accurate first principles BO MD simulations at a fraction of the cost of regular simulations. The third publication presents a generalized framework for a new generation extended Lagrangian BOMD that allows stable integration in the limit of vanishing SCF optimization for a

broader class of materials. The framework has some remarkable features, apart from a more rigorous derivation. Geometric integration schemes, like the velocity Verlet algorithm, can be understood from a backward analysis. Instead of an approximate integration, a geometric integration allows an exact integration of an underlying approximate shadow dynamics. In the same way, the generalized framework allows an exact integration with exact forces that are calculated in a single step (instead of using multiple SCF iterations) for an underlying approximate shadow Hamiltonian. We have developed the concept of a shadow Hamiltonian also for SCF theory. This approach opens the door to new applications, including fast MD formulations for orbital-free DFT and polarizable force fields.

Discontinuous Methods for Massively Parallel QMD: Li-ion Interface Dynamics from First Principles

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Funding: \$361,000 (2014)

Jointly funded by the Chemical Sciences, Geosciences, & Biosciences Division and Materials Sciences and Engineering Division

PROGRAM SCOPE

We develop and employ for the first time new Discontinuous Galerkin (DG) and Pole Expansion/Selected Inversion (PEXSI) electronic structure methods to accomplish quantum molecular dynamics (QMD) on an unprecedented scale; and apply the new methodologies to address fundamental questions in energy storage: the formation and evolution of the solid-electrolyte interphase (SEI) layer in Lithium-ion cells. We employ state-of-the-art massively parallel planewave codes in the initial phase of the work while the new DG and PEXSI methodologies are developed and verified. We then apply the new methodologies to much larger systems, up to 10,000 atoms, in order to reach for the first time sufficient system complexity to effectively model complete liquid-on-anode configurations. The remarkable properties of the new methodology are made possible by releasing the constraint of continuity through the DG formulation of the Kohn-Sham equations. By virtue of these properties, our initial parallel implementation has accomplished *ab initio* calculations with over 4,000 atoms with planewave accuracy. Initial DG QMD simulations show excellent energy conservation, with energy drift < 2 meV/atom/ps. To reach the largest system sizes, we develop and employ the new PEXSI methodology, eliminating the need for diagonalization while retaining strict systematic improvability and applicability to both metals and insulators. In partnership with the SciDAC FASTMath Institute, we have completed MPI parallelization of the PEXSI code, testing on a wide range of systems, documentation, and release (<http://www.pexsi.org>). The resulting code can scale to over 100,000 processors and has now been applied to systems containing over 45,000 atoms. Current work focuses on the combination of DG and PEXSI methodologies to reach the length and time scales necessary to model mixed-phase anode-electrolyte configurations to begin to understand for the first time the chemistry and dynamics at this critical interface.

FY 2014 HIGHLIGHTS

We accomplished all FY14 project milestones and commenced work on FY15 milestones. Four journal articles were published and five more submitted. We carried out an extensive series of QMD simulations of ethylene carbonate (EC), ethyl methyl carbonate (EMC), and EC/EMC mixture solvents with LiPF₆ salt, as widely used in practice. We found that Li prefers tetrahedral coordination in all electrolytes considered, consistent with experiment for EC, and providing a prediction for EMC and EC/EMC mixture. Most significantly, we found a key correlation of solvation and mobility in all electrolytes considered: the stronger the solvation, the less the mobility. This finding has the potential to significantly impact the engineering and improvement of Li-ion battery electrolytes going forward, and with that, battery systems as a whole. Regarding the new Discontinuous Galerkin (DG) computational methodology being developed to reach the needed length and time scales to model full anode-electrolyte systems, we made a number of advances. We implemented independent grids for density and wavefunctions, yielding accurate forces for all atomic species, soft and hard, metals and nonmetals alike. We implemented molecular dynamics, obtaining excellent energy conservation. We implemented MPI parallelization of local Kohn-Sham solves to form DG basis in each element, yielding a 70-fold speedup. Regarding the new Pole Expansion and Selected Inversion (PEXSI) methodology being developed to eliminate the need for diagonalization altogether, we parallelized, tested, documented, and released a full production code (<http://www.pexsi.org>). The new MPI code scales to over 100,000 CPUs. The new PEXSI code has been incorporated into the widely used SIESTA electronic structure code, yielding a factor of 18 speedup. Finally, we implemented the new PEXSI methodology with the DG basis to reach the largest length and time scales needed to model full anode-electrolyte configurations.

Molecular Theory and Modeling

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Funding: \$2,260,000 (2014)

PROGRAM SCOPE

We seek a fundamental understanding of important processes such as solvation, transport, and reaction in complex condensed-phase and interfacial environments. This research provides a basis for the development of new and improved energy technologies and the control of environmental impacts of energy use. We have focused on processes in aqueous solutions, interfacial water, ionic liquids, and molecular frameworks. We systematically connect processes in simpler to increasingly more complex systems and advance fundamental understanding of molecular systems through the development of molecular modeling methods. This includes the construction of models of molecular interaction based on empirical forms as well as explicit electronic structure. We combine this development with appropriate statistical and dynamical sampling techniques to elucidate fundamental properties and

behavior of well-characterized systems for benchmarking by experimental measurement. With an established knowledge of fundamental processes, we better understand the ability to control and design processes in more complex systems where complexity is due to heterogeneity in space or time scales.

FY 2014 HIGHLIGHTS

The group has made significant steps towards an improved understanding and characterization of the solvation of ions by developing and combining models of molecular interaction, electronic structure and statistical mechanics. These approaches have been benchmarked by experimental measurement using X-ray absorption, optical vibrational and photoelectron spectroscopies. We have examined the consequences of empirical models on the dynamics of the ion-pairing process. To this end, sound theoretical protocol is used to not only compute rates of ion pairing but also determine the important and measurable excess molar volumes. These studies provide the development of stringent tests for the accuracy of pair potentials to be used in complex processes such as nucleation. We are developing a molecular understanding of the non-linearity that give rise to solvation. Our research will go beyond the phenomenology of the Born model to theoretically account for the explicit short-range response giving rise to free energies of solvation. An exciting consequence of this research is that it will, in general, be model dependent and will take full advantage of our current research on connecting molecular detail to the measured hydration structure using the molecular dynamics – extended X-ray absorption fine structure (MD-EXAFS) approach. We are developing a framework of universal potential energy functions to describe intermolecular interactions from the very weak to the very strong. In addition, we are modeling the electronic states of multivalent metals and their variation with the degree of aqueous solvation. We have combined theoretical and experimental photoelectron spectroscopy characterizations of solvated clusters, confirming the importance of local solvent structure in regulating solute specific effects.

Pressure Dependence of Combustion Reactions: Quantum Inelastic Dynamics on Automatically Generated Potential Energy Surfaces

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Sr. Investigator(s):
Students: 0 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding: \$422,000 (2014)

PROGRAM SCOPE

This project studies the pressure-dependence of combustion reactions, in part by developing and using high quality potential energy surfaces (PES). This project has evolved in two directions. The first is classical molecular dynamics studies of excited molecules in a buffer gas at pressures high enough so that isolated binary collisions are unusual. This requires explicit simulation of both the molecule and the buffer gas. At pressures relevant to advanced internal combustion engines, energy relaxation rates can no longer be directly proportional to pressure and the mechanisms that lead to this are a focus of the study. The second and unexpected direction that arose out of working with high quality potential energy surfaces is the development of second order vibrational perturbation theory (VPT2) to derive tunneling probabilities. I have modified semiclassical tunneling methods that use VPT2 results, thereby enabling their calculation of deep tunneling. Such methods may offer a fast alternative to reaction path following

tunneling methods because VPT2 calculations are readily parallelized but most methods to characterize reaction paths are sequential in character. This project involves collaborations with others in BES in PES development and use and with the Thompson group (U. Missouri) in molecular dynamics studies.

FY 2014 HIGHLIGHTS

1. An energy relaxation study of excited CH_3NO_2 in an Ar bath gas by classical molecular dynamics techniques was carried out over a pressure range of 10 to 400 atm. At all pressures a Lendvay-Schatz fit accurately represented the relaxation rate in terms of an initial rate k_i and an "m" parameter describing the curvature on a semi-log plot of energy versus time. k_i is not directly proportional to pressure for pressures beyond ~ 100 atm. A combinatorial model was developed to account at higher pressures for the molecule undergoing multiple simultaneous Ar collisions and this model could be adjusted to fit the k_i pressure dependence. That fit suggested that N multiple collisions are not as efficient as N single collisions, resulting in a changing pressure dependence. A paper describing this has just been published in FY15.
2. An improved semiclassical tunneling theory based on second order vibrational perturbation theory was published at the beginning of FY14 and tested on multiple potentials of HOCO in a second paper in FY14. The tests show good comparisons with tunneling probabilities from reaction path following methods and, with the best of four potential energy surfaces, good comparisons with experiment.

Condensed Phase and Interfacial Molecular Science

Institutions Receiving Grants

Transition Metal-Molecular Interactions Studied with Cluster Ion Infrared Spectroscopy

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Students: 0 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding: \$136,000 (2014)

PROGRAM SCOPE

Transition metal ion-molecular complexes are studied in the gas phase to investigate the fundamental interactions in catalysis, metal-ligand bonding and metal ion solvation. Cation-molecular complexes of the form $M_x^{n+}(L)_y$, where M= transition metals (Fe, Co, Ni, Cu, etc.) in singly or multiply charged states, and L= small molecules such as CO, CO₂, O₂, H₂O or benzene, are produced in a molecular beam by pulsed laser vaporization of solid metal targets. Complexes containing a specific number of metal atoms and ligands are cooled by a supersonic expansion, size-selected in a reflectron time-of-flight mass spectrometer, and studied with infrared laser photodissociation spectroscopy. The resulting vibrational spectra reveal the shifts that occur for ligand/adsorbate vibrations upon binding to metal, how this varies with the number of ligands, the geometric and electronic structures of complexes, the number of ligand/solvent molecules in the full coordination sphere around the metal, and the possible occurrence of ligand reactions mediated by the metal center. New experiments employ photofragment imaging technology to further investigate low frequency vibrations and metal-molecular bond energies. The experimental work is elucidated and complemented by density functional theory computations. The increased understanding of fundamental metal interactions impacts diverse areas such as heterogeneous and homogeneous catalysis, solar energy generation, hydrogen storage, CO₂ sequestration, and nuclear waste management.

FY 2014 HIGHLIGHTS

Ongoing experiments have employed infrared laser photodissociation methods to measure infrared spectroscopy of metal ion-water and metal ion-benzene complexes. Computational chemistry was employed to predict structures, electronic states and vibrational spectra for these systems. In a major new direction, a modified mass spectrometer system was constructed and implemented for photofragment imaging of the decomposition products resulting when metal ion complexes dissociate. The new instrument produces cold ions, selects them by mass, and dissociates them on electronic or vibrational resonances. Velocity map imaging and slice imaging methods provide high resolution images, yielding new and improved thermochemistry for a variety of metal ion-molecule complexes.

Confinement, Interfaces, and Ions: Dynamics and Interactions in Water, Proton Transfer, and Room Temperature Ionic Liquid Systems

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Students: 0 Postdoctoral Fellow(s), 3 Graduate(s), 0 Undergraduate(s)
Funding: \$270,000 (2014)

PROGRAM SCOPE

A variety of topics are being addressed that have a common theme, that is, the relationship between dynamics, structure, and interactions in systems that are structurally heterogeneous on mesoscopic distance scales. The studies are addressing a variety of chemical and materials systems. Room temperature ionic liquids (RTIL) are organized into ionic and organic regions. Water is found in nanoconfined materials such as polyelectrolyte fuel cell membranes, which have nanoscopic channels that contain water and conduct protons, liquids in porous SiO₂ and porous SiO₂ particles functionalized with a heterogeneous photocatalyst, water in reverse micelles, and proton transfer in nanoconfined systems, particularly fuel cell membranes and reverse micelles. Porous SiO₂ functionalized with a homogeneous catalyst to form a heterogeneous catalyst have dynamics dictated by the proximity of the surface and interactions with nanoconfined solvents. RTILs, which are becoming important in batteries and other applications, segregate into ionic and organic regions on nanometer length scales. Water occurs in many nanoconfined systems, where its properties differ greatly from bulk water. Mesoscopically structured systems are being studied with ultrafast 2D IR vibrational echo methods. 2D IR is akin to 2D NMR but it operates on times scales that are ten orders of magnitude faster than NMR. 2D IR experiments make it possible to observe dynamics of complex molecular systems on the time scales of the fundamentally important events. IR polarization selective pump-probe experiments are being used to measure molecular orientational relaxation and vibrational lifetimes, which provide a detailed view of the relationships between structure and dynamics. Optical heterodyne detected optical Kerr effect experiments and fast fluorescence experiments are also important techniques being used in the study dynamics and structure in the mesoscopically structured systems.

FY 2014 HIGHLIGHTS

Ultrafast 2D IR vibrational echo experiments have been applied to the study of room temperature ionic liquids to understand the dynamics and nature of water and small alcohols, i. e., methanol and ethanol solutes, in the RTILs. IR pump-probe experiments were also used to measure orientational relaxation. The dynamics observed with 2D IR slow only slightly as the solute gets larger although the orientational relaxation time slows a good deal as the solute size increases. In addition, 2D IR experiments have been used to study the dynamical interactions of dihydrogen bonded ions with water. In particular, borohydride dihydrogen bonded to water was examined both from the perspective of water bound to borohydride using the dihydrogen bonded hydroxyl stretch as the vibrational probe, and from the system “inside” the anion using the B-H stretch of borohydride as the probe. In addition, IR pump-probe orientational relaxation measurements were made on this system. The remarkable results show that the hydrogen bond dynamics in concentrated NaBH₄ systems are virtually identical to those of pure water, in contrast to other concentrated salt solution. It is proposed that the limited affect of borohydride on water dynamics occurs because borohydride provides a tetrahedral hydrogen bonding arrangement. Proton transport in water, ionic and non-ionic reverse micelles, and several fuel cell polyelectrolyte membranes were investigated. Proton transport is studied by measuring the fast fluorescence from a photoacid placed in each type of system. A new theory that properly extracts the proton transfer dynamics from the time dependent fluorescence spectroscopy of the protonated and

deprotonated emission band of the photoacid was developed. Proton transfer in the nanoconfined water in ionic and neutral reverse micelles are fundamentally different. Differences in proton transfer in fuel cell membranes made by different companies are also beginning to be observed.

EARLY CAREER: Probing Chromophore Energetics and Couplings for Singlet Fission in Solar Cell Applications

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Students: 0 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding: \$141,000 (2014)

PROGRAM SCOPE

The goal of this project is to provide a molecular-level understanding of processes that can improve efficiencies of alternative sources of energy, such as dye-sensitized solar cells. In particular, the mechanisms and molecular requirements for efficient exciton multiplication through singlet fission are explored using high-resolution anion photoelectron (PE) spectroscopy. The experiments are capable of observing directly the singlet, triplet, and charge transfer states involved in singlet fission and determining precisely their energetics, vibrational structures and couplings. More specific aims are (1) to probe the evolution of the electronic structure as a function of cluster size in order to understand singlet fission in crystals, (2) to explore the relationship between the nature of linkers and the electronic structure in covalently-bonded chromophore dimers, and (3) to highlight the differences, including exciton delocalization and the effects of solvent interactions, between the crystalline species and the isolated covalently-bonded dimers. The electronic states of organic chromophore clusters and covalently-bonded dimers will be probed via high-resolution photoelectron spectroscopy (SEVI) of mass-selected radical anion precursors. Specifically, starting with the radical anion with a doublet ground state, all the low-lying singlet and triplet states of the neutral molecule that involve removal of a single electron can be accessed in the one-photon experiment. Therefore, with the exception of the doubly excited state, all the electronic states relevant to singlet fission will be accessible. Using anions also provide the added advantage of mass selection, which is crucial for studying the behavior of singlet fission as a function of cluster size.

FY 2014 HIGHLIGHTS

Since the beginning of this program in July 2013, we have started to design and build the cryogenic SEVI setup. Currently, the electrospray source, the ion guides, the main quadrupole ion trap, and the time-of-flight mass spectrometer has been built, and the assembly process is almost complete. At the same time, simulations and designing of the VMI stage is being carried out to achieve optimal signal-to-noise ratio and energy resolution. Conventional VMI setup has two main issues that are amplified when the method is applied to low energy electrons. Namely, spherical aberration causes electrons with different kinetic energies to have different focal points, and electrons ejected from VMI electrodes can cause significant background noise in the image. The latter becomes particularly overwhelming when the photon energy exceeds the work function of the electrode, which is often a necessity when probing excited electronic states. A new multiple-electrode VMI is being designed that should simultaneously alleviate both problems, giving the SEVI apparatus a wider applicability. We also began investigating the

formation of the polyacene radical anion directly from electrospray ionization using a separate already operational cryogenic ion vibrational spectrometer. Two different approaches are being tested. In one method, a strong reducing agent is added to the polyacene solution, where a faint color change can be observed indicating the polyacene has been reduced. Electrospray of the reduced solution has yielded radical anion signals, however source conditions need to be optimized for signal stability. The other method utilizes electrochemistry to controllably reduce the polyacene species, many of which has known redox potentials.

Ultrafast Molecular Scale Chemical Imaging

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Funding: \$600,000 (2014)

PROGRAM SCOPE

This SISGR program utilizes recently developed instrumentation including integrated ultra-high vacuum tip-enhanced Raman spectroscopy/scanning tunneling microscopy (UHV-TERS/STM) and surface-enhanced femtosecond stimulated Raman scattering (SE-FSRS) to advance the spatial and temporal resolution of chemical imaging for the study of photoinduced dynamics of molecules on plasmonically active surfaces. For example, UHV-TERS/STM at liquid helium temperatures achieves unprecedentedly high spectral resolution, which allows the conformation of adsorbates to be deduced with respect to surface features such as atomic step edges. The UHV environment also minimizes adsorbate degradation at high laser intensities, thus enabling TERS to be performed with ultrafast excitation. A wide range of materials and adsorbates are being studied including chemically functionalized graphene, two-dimensional silicon, and organic donor-acceptor molecular heterostructures. An accompanying theory program includes modeling of charge and energy transfer processes using constrained density functional theory, thereby providing a detailed description of excited state dynamics. Overall, this SISGR program directly addresses the DOE BESAC Grand Challenges by realizing fundamental advances such as: (a) Characterization of chemical reactions with unprecedented spatial and temporal resolution; (b) Improved understanding of optical interactions with nanoscale materials; (c) Development of new optically active materials; (d) Establishment of a powerful platform for studying photochemistry on atomically engineered surfaces. Technologically, these fundamental developments impact efforts to extract useful energy from solar radiation including: (a) Photovoltaic devices; (b) Artificial photosynthesis; (c) Photocatalytic materials.

FY 2014 HIGHLIGHTS

Over the past year, significant experimental and theoretical progress has been made on multiple topics including ultrafast UHV-TERS/STM and chemically modified graphene and silicon on plasmonic substrates:

- (1) Ultrafast UHV-TERS/STM: The SISGR team reported the first UHV-TERS data with liquid helium cooling of the sample, from which the adsorbate-substrate interactions of the rhodamine

6G/Ag(111) system were quantified. In particular, the spectra exhibited significant line narrowing up to the instrument-limited response along with new vibrational characteristics of rhodamine 6G that were identified through theoretical analysis. Temporally resolved TERS was also advanced by incorporating picosecond pulses into the UHV-STM for pulsed-excitation UHV-TERS. UHV-TERS spectra of rhodamine 6G on Ag(111) were gathered using picosecond irradiation and, importantly, these experimental results show that the UHV environment mitigates signal decay.

- (2) Chemically Modified Graphene and Silicon on Plasmonic Substrates: The SISGR team achieved the first growth of graphene on Ag(111). Since traditional chemical vapor deposition techniques that are typically utilized for graphene growth do not work on Ag substrates, an alternative method was developed based on direct deposition of elemental carbon. In an effort to diversify the range of surface chemistries on plasmonically active substrates, the SISGR team also completed an extensive study that follows the evolution of silicon deposition on Ag(111) from multiple surface alloy phases to the precipitation of two-dimensional sheets of crystalline silicon. This silicon growth method is compatible with graphene growth on silver, which facilitates the synthesis of both lateral and vertical graphene-silicon heterostructures. These substrates allow direct interrogation of the interaction of adsorbates with two contrasting surfaces: highly reactive silicon and relatively inert graphene.

Spectroscopic Imaging of Molecular Functions at Surfaces

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Funding: \$501,000 (2014-2016)

PROGRAM SCOPE

The functions of a molecule depend on its composition, structure, and environment. The composition is determined by identifying the atoms in the molecule. The arrangement of the atoms gives its structure. The changes that the molecule undergoes are in response to its environment, such as temperature, light, charge, and other chemical species. The proposed research seeks an understanding of molecular functions by relating them to the composition, structure, and environment with low temperature scanning tunneling microscopes (STM). Recent advances with the STM in real-space imaging of molecular structure by resolving each atom and bond in a molecule, combined with electronic and vibrational spectroscopies and manipulation, provide renewed opportunities to understand molecular functions at the single molecule level. The relationships between structure and bonding are central for understanding chemistry in the proposed study. The proposed research focuses on four key problems in chemistry: 1. the nature of hydrogen bonding, 2. the mechanisms of tautomerism, 3. molecular responses to environmental changes, and 4. the nature of the chemical bond and interactions. In addition to obtaining fundamental understanding and control of interfacial chemistry, knowledge gained from these experiments provide the scientific basis for technologies, such as heterogeneous catalysis, organic solar cells, environmental remediation, water management, alternative energy, and green chemistry.

FY 2014 HIGHLIGHTS

A new and generally applicable technique based on the scanning tunneling microscope (STM) explains the origin of the ball-and-stick representation of molecules and relates structure to function. Images of chemical bonds by the inelastic tunneling probe (itProbe) reveal molecular structure and multi-centered hydrogen bonding. A tip terminated with a single carbon monoxide (CO) molecule was scanned over a single cobalt-phthalocyanine (CoPc) molecule adsorbed on Ag(110) surface at 600 mK while monitoring the hindered translational vibration of the CO by inelastic electron tunneling spectroscopy (IETS). The variations in the vibrational intensity in the scan provide the contrast in the CoPc skeletal structure due to the CO molecule sensing the repulsive potential of CoPc. The energy, intensity, and line shape of the CO vibration are sensitive to the skeletal structure in the molecule [cobalt phthalocyanine (CoPc): 57 atoms, 68 bonds, and 4 lone pairs] and its surrounding. The CO vibration senses the skeletal structure differently than elsewhere, and is detected by STM-IETS at 600 mK. The itProbe is expected to be generally applicable to other molecules. In addition to providing an understanding of the scientific basis for the ball-and-stick model, itProbe is used to obtain new insights into intramolecular and extramolecular hydrogen bonding. Specifically, hydrogen atoms can be shared among a larger number of centers to form three-center two-hydrogen intramolecular hydrogen bonds within a CoPc molecule, five-center four-hydrogen intermolecular hydrogen bonds between two CoPc molecules, and three-center one-hydrogen bonds with the substrate. The structural images reveal intra- and extramolecular multicenter bonds involving hydrogen. Direct visualization of the bifurcated hydrogen bonding provides an understanding into the relation of structure and function in self-assembly, biological molecules, and chemistry.

Theory of the Reaction Dynamics of Small Molecules on Metal Surfaces

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Principal Investigator: Bret Jackson
Sr. Investigator(s):
Students: 0 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

Our objective is to develop realistic theoretical models for molecule-metal interactions important in catalysis and other surface processes. Recent efforts have focused on the dissociative chemisorption of methane on metal surfaces, the rate-limiting step in the chief industrial process for production of H₂. Initial studies of methane dissociation on Ni(111) and Ni(100) used DFT to compute barrier heights and explore the potential energy surface for this reaction, with an emphasis on how it changes due to lattice motion. We found that when the Ni atom over which the molecule dissociates vibrates in and out of the plane of the surface, the barrier to dissociation changes. Quantum scattering calculations showed that this leads to a strong increase in reactivity with temperature. Subsequent studies on Pt(111), Pt(100) and Pt(110)-(1x2) found similar behavior. We have developed sudden models that accurately add the effects of thermal lattice motion to static-lattice calculations. We have explored the dynamics of methane dissociation using a formulation based on the Reaction Path Hamiltonian. We first locate the reaction (minimum energy) path for dissociation, and perform a normal mode analysis at several points along this path. This generates a full-dimensional description that includes all 15 degrees of freedom of the methane. Time-dependent quantum dynamics based on this Hamiltonian were used to examine

methane dissociation on Ni(100), Ni(111), and the highly-corrugated Pt(110)-(1x2). Agreement with experiment was good with respect to the magnitude of the reactivity and its variation with translational energy and the vibrational state of the methane. More importantly, the ability to examine the flow of energy between the various molecular and lattice degrees of freedom during the reaction has allowed us to learn much about the reaction dynamics, and mode-selective chemistry in particular.

FY 2014 HIGHLIGHTS

We explored the dissociative adsorption of methane on Ni(100) and Ni(111) using a classical form of the Reaction Path Hamiltonian. This allowed us to test approximations used in our quantum model, and to examine the limitations of classical methods. Our quantum perturbative assumption was shown to be highly accurate, and we found that the large amount of zero point vibrational energy in the molecule led to errors in the reaction probability for ground state molecules at low translational energies. Working with the Kroes group (Leiden) we used *ab initio* molecular dynamics to study methane dissociation on Pt(111) and Ni(111). In this classical approach forces are computed “on the fly”, via DFT. The surfaces were modeled with large dynamical slabs, and energies and temperatures were chosen to avoid errors due to the use of classical mechanics. As part of a 4-way interaction, experiments were performed at these same energies and temperatures by the Utz (Tufts) and Beck (EPFL) groups. One goal was to test the accuracy of different density functionals and van der Waals treatments, and develop more accurate functionals. Another was to better understand the dynamics of these reactions. We found that our sudden treatment of molecular translation parallel to the surface was very reasonable, but that the rotational dynamics were closer to sudden than adiabatic. Using what we learned in these studies, we significantly improved the treatment of molecular rotation in our quantum model, and significantly expanded our vibrational basis set. In a new and more detailed study of methane chemisorption on Ni(111) we found excellent agreement with some new data from the Utz lab, and were able to explain why the temperature dependence of the reaction differed so dramatically above and below an energy threshold. Most recently we have begun to examine mode-specific and bond-selective chemistry in the reactions of CHD₃ and CH₂D₂ on Ni(111).

Probing Catalytic Activity in Defect Sites in Transition Metal Oxides and Sulfides Using Cluster Models: A Combined Experimental and Theoretical Approach

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Funding: \$180,000 (2014)

PROGRAM SCOPE

Our research program combines experimental and computational methods to study well-defined cluster models of heterogeneous catalytic materials. The focus has been transition metal oxide and sulfide clusters in non-traditional oxidation states (surface defect models) and their chemical and physical interactions with water, with the goal of modelling and understanding the role of various processes involved in H₂ production from photocatalytic decomposition of water using Group 6 (Mo and W) oxides and sulfides. The experiments and calculations are designed to probe fundamental, cluster-substrate molecular-scale interactions that are governed by charge state, peculiar oxidation states, and unique

physical structures. The general strategy of our studies is as follows: (1) Determine how the molecular and electronic structures of transition metal suboxide and subsulfide clusters evolve as a function of oxidation state by reconciling anion photoelectron spectra of the bare clusters with high-level DFT calculations. Anions are of particular interest because of the propensity of metal oxide and sulfides to accumulate electrons in applied systems. (2) Measure and analyze the kinetics of cluster reactions with water. (3) Dissect possible reaction mechanisms computationally to determine whether catalytically relevant interactions are involved. (4) Verify the computational studies by anion photoelectron spectroscopic investigation of observed reactive intermediates. (5) Probe the effect of local electronic excitation on bare clusters and cluster complexes, to evaluate photocatalytic processes. The overarching goal of this project is to identify particular defect structures that balance structural stability with electronic activity, both of which are necessary for a site to be simultaneously robust and catalytically active, and to find trends and patterns in activity that can lead to improvement of existing systems, or the discovery of new systems.

FY 2014 HIGHLIGHTS

We have a series of successful computational and experimental studies on tungsten and molybdenum oxides and sulfides, along with their interactions with water, that have led to six publications in fiscal year 2014, with several additional manuscripts in preparation. We have completed a series of experimental reactivity studies and computational studies on mechanisms and energies for the $M_xO_y + H_2O$ ($M = Mo, W; x = 2, 3; y < 3x$) reactions from which we have probed the interplay between electrostatic interactions, oxygen vacancies, M-O bond energies, and subtle differences in barrier heights on cluster-water interactions. Of note is the importance of strong dipole-dipole interactions, which are more important than charge-dipole interactions in initiating water decomposition. From past studies, proton mobility featured prominently in the decomposition mechanism. We have subsequently completed several cluster-alcohol reactivity studies to evaluate this finding. Metal sulfide clusters proffer different mechanisms for water decomposition with H_2 production relative to their oxide analogs. Specifically, dithiol complexes can lead to H_2 evolution. Additionally, calculations mixed metal sulfide clusters predict higher chemical activity toward water decomposition. Finally, we have initiated temperature-dependence studies on cluster-water reactions, and have measured size- and composition-dependent anti-Arrhenius behavior that can be correlated with low-barrier interactions between the clusters and water, along with entropic factors.

Critical Evaluation of Theoretical Models for Aqueous Chemistry and CO_2 Activation in the Temperature-Controlled Cluster

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Principal Investigator: Mark Johnson
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Students: 1 Postdoctoral Fellow(s), 4 Graduate(s), 0 Undergraduate(s)
Funding: \$120,000 (2014)

PROGRAM SCOPE

Our program exploits strongly coupled experimental (Johnson at Yale) and theoretical (Jordan at Pittsburgh) studies of size-selected clusters as a medium with which to unravel molecular level pictures of key transient species in condensed phase and interfacial chemistry that are relevant to radiation

damaged systems as well as to catalytic activation of carbon dioxide for conversion into transportable fuels. Much of this work involves trapping labile free radicals created using negatively charged, gas phase molecular clusters as powerful reducing agents. On the experimental side, this is carried out using custom built apparatus, under DOE support, of cryogenic ion trapping methods interfaced with ambient ionization sources that allow direct access to species with very low vapor pressure and that indeed sometimes only exist when surrounded by solvent. Our current focus is on the elementary processes underlying the elementary steps by which proton-coupled electron transfer through water networks mediates electron capture onto secondary molecular electron scavengers. Part of this effort necessarily involves understanding the speciation of an excess proton in restricted hydration environments. Our approach is to unravel how an excess proton reports on the nature of its local environment through its vibrational signature in the infrared region of the spectrum. Here the coupling between theory and experiment has been crucial and effective, as these signatures are often quite complex, requiring the introduction of new theoretical methods to explain their quantum mechanical origins. An emerging direction for our work involves understanding the molecular-level interactions between components in room temperature ionic liquids (ILs), as these media are increasingly used for “green chemistry” and as solvents for carrying electrochemical conversion of carbon dioxide.

FY 2014 HIGHLIGHTS

The major advance in this fiscal year has been a breakthrough regarding the identification of the spectral signature of an excess proton trapped in a three-dimensional, cage-like water cluster. Although the nature proton accommodation by smaller water networks ($n < 11$) is now well established from our work a decade ago, the extension of those measurements to sufficiently large clusters to accurately mimic bulk behavior has proven to be remarkably difficult. It was therefore a major advance in the spring of 2014, when we succeeded in obtaining a D_2 predissociation spectrum of the $n=21$ “magic number” cluster, and analyzing the structural implications of it with anharmonic calculations of the vibrational spectra predicted for various possible cluster geometries. The first paper describing these results was published in *Science* in 2014, and was highlighted in *Chemistry World* (<http://www.rsc.org/chemistryworld/2014/05/water-cluster-structure-proton-acid>) and *Yale News* (<http://news.yale.edu/2014/06/05/case-closed-where-missing-proton-goes>). We immediately followed this paper with a second Communication in the *Journal of Chemical Physics* where we minimized the extent of the structural distortion introduced by the relatively strongly bound D_2 molecule in the first measurement by replacing it with an extremely weakly bound helium atom. A third paper was also submitted to *Proceedings of the National Academy of Sciences* reporting the identification of the cage structure type by assigning particular features in the OH stretching region to specific hydrogen bonding sites in the network. A second major advance in this fiscal year has been our definitive study quantifying the role of hydrogen bonding in ionic liquids based on the commonly used imidazolium cation.

Critical Evaluation of Theoretical Models for Aqueous Chemistry and CO_2 Activation in the Temperature-Controlled Cluster Regime

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Principal Investigator: Kenneth Jordan
Sr. Investigator(s):
Students: 1 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding: \$115,000 (2014)

PROGRAM SCOPE

Our program exploits strongly coupled experimental (Johnson at Yale) and theoretical (Jordan at Pittsburgh) studies of size-selected clusters as a medium with which to unravel molecular level pictures of key transient species in condensed phase and interfacial chemistry that are relevant to radiation damaged systems as well as to catalytic activation of carbon dioxide for conversion into transportable fuels. Much of this work involves trapping labile free radicals created using negatively charged, gas phase molecular clusters as powerful reducing agents. On the experimental side, this is carried out using custom built apparatus, under DOE support, of cryogenic ion trapping methods interfaced with ambient ionization sources that allow direct access to species with very low vapor pressure and that indeed sometimes only exist when surrounded by solvent. Our current focus is on the elementary processes underlying the elementary steps by which proton-coupled electron transfer through water networks mediates electron capture onto secondary molecular electron scavengers. Part of this effort necessarily involves understanding the speciation of an excess proton in restricted hydration environments. Our approach is to unravel how an excess proton reports on the nature of its local environment through its vibrational signature in the infrared region of the spectrum. Here the coupling between theory and experiment has been crucial and effective, as these signatures are often quite complex, requiring the introduction of new theoretical methods to explain their quantum mechanical origins. An emerging direction for our work involves understanding the molecular-level interactions between components in room temperature ionic liquids (ILs), as these media are increasingly used for “green chemistry” and as solvents for carrying electrochemical conversion of carbon dioxide.

FY 2014 HIGHLIGHTS

Much of our early effort has been directed at understanding how the shape of the water network controls the excess electron binding properties. During the present grant period, we have completed a long-standing goal of experimentally isolating the spectral contributions of water molecules in individual network sites to the broad vibrational envelope, and established bounds on the barriers separating the different isomers by measuring the energy dependences of their photochemical interconversions. Midway through this period, we began expanding the scope of our work beyond water to explore the excess electron-driven proton transfer event at the heart of free radical formation in radiation-induced DNA damage. Most recently, we exploited the methodologies we have developed over several years of DOE support to initiate a series of studies aimed at understanding the molecular level processes underlying reductive CO₂ activation in the development of solar fuels. After a brief review of these advances, we outline exciting opportunities both in the basic science of aqueous chemistry and in molecular level aspects of CO₂ activation in ionic liquids.

Probing Ultrafast Electron (De)localization Dynamics in Mixed Valence Complexes Using Femtosecond X-ray Spectroscopy

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Robert Schoenlein; Lawrence Berkeley National Laboratory
Shaul Mukamel; California-Irvine, University of
Students: 3 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding: \$700,000 (2014)

PROGRAM SCOPE

The goal of this recently funded project (started on 9/1/2014) is to directly measure photoinduced electron delocalization/localization dynamics on a sub-50 fs timescale at the atomistic level in a series of solvated transition metal mixed valence complexes. The experiments will utilize the femtosecond X-ray pulses at LCLS (XPP/SXR instruments) to perform femtosecond X-ray absorption, emission and resonant inelastic X-ray scattering (RIXS) spectroscopies following photoexcitation of the sample. This study will aim to understand valence electron motion following metal-to-metal charge transfer (MMCT) excitation in mixed valence complexes. In the chosen complexes, the communication between the two metal atoms is varied by changing the identity and oxidation state of the metal atom and varying the ligand shell surrounding the metal atom. The chosen complexes provide a rich molecular playground to study the effects of electronic coupling, delocalization and electron-nuclear coupling between two transition metals connected with a cyanide bridge. The ultrafast X-ray experiments will be performed by the Khalil and Schoenlein group members and will allow for an unprecedented view of the motion of the valence electrons between the metal centers and subsequent electronic and structural relaxation following MMCT. The success of the experiments will depend on the ability to interpret the core-level spectra of the photo-excited states of electron-rich transition metal molecular systems in solution. The experiments will be combined with theoretical X-ray spectroscopic and ultrafast electronic dynamics simulations performed by the Govind and Mukamel group members. The results will provide a molecular-level understanding of “the extent of electron delocalization” during a photoinduced chemical reaction, which remains a fundamental question in the field of mixed valence chemistry and crucial to designing mixed valency in supramolecular complexes and in molecular electronics.

FY 2014 HIGHLIGHTS

The project was started on September 1, 2014. Given the start date, there are no significant accomplishments to report in the fiscal year 2014.

Single-Molecule Interfacial Electron Transfer

Institution: Bowling Green State University
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Sr. Investigator(s):
Students: 2 Postdoctoral Fellow(s), 1 Graduate(s), 1 Undergraduate(s)
Funding: \$338,000 (2014)

PROGRAM SCOPE

Our research at the Photochemical Sciences Center and Department of Chemistry, Bowling Green State University, is focused on the use of single-molecule high spatial and temporal resolved techniques to study molecular dynamics in condensed phase and at interfaces, especially, the complex reaction dynamics associated with electron and energy transfer rate processes. The complexity and inhomogeneity of the interfacial ET dynamics often present a major challenge for a molecular level comprehension of the intrinsically complex systems, which calls for both higher spatial and temporal resolutions at ultimate single-molecule and single-particle sensitivities. Combined single-molecule spectroscopy and electrochemical atomic force microscopy approaches are unique for heterogeneous and complex interfacial electron transfer systems because the static and dynamic inhomogeneities can

be identified and characterized by studying one molecule at a specific nanoscale surface site at a time. The goal of our project is to integrate and apply these spectroscopic imaging and topographic scanning techniques to measure the energy flow and electron flow between molecules and substrate surfaces as a function of surface site geometry and molecular structure. We have been primarily focusing on studying interfacial electron transfer under ambient condition and electrolyte solution involving both single crystal and colloidal TiO₂ and related substrates. The resulting molecular level understanding of the fundamental interfacial electron transfer processes will be important for developing efficient light harvesting systems and broadly applicable to problems in fundamental chemistry and physics.

FY 2014 HIGHLIGHTS

We have made significant advancement on deciphering the underlying mechanism of the complex and inhomogeneous interfacial electron transfer dynamics in dye-sensitized TiO₂ nanoparticle systems that strongly involves with and regulated by molecule-surface interactions. We have studied interfacial electron transfer on TiO₂ nanoparticle surfaces by using ultrafast single-molecule spectroscopy and electrochemical AFM metal tip scanning microscopy, focusing on understanding the interfacial electron transfer dynamics at specific nanoscale electron transfer sites with high-spatially and temporally resolved topographic-and-spectroscopic characterization at individual molecule basis, characterizing single-molecule rate processes, reaction driving force, and molecule-substrate electronic coupling. One of the most significant characteristics of our new approach is that we are able to interrogate the complex interfacial electron transfer dynamics by actively pin-point energetic manipulation of the surface interaction and electronic couplings, beyond the conventional excitation and observation.

Dynamics Studies of Photo- and Electron-Induced Reactions on Nanostructured Surfaces

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Students: 1 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding: \$369,000 (2014-2016)

PROGRAM SCOPE

Photoexcitation has been of continuing interest for its importance in several methods of solar-energy conversion, in photocatalytic destruction of environmental pollutants, and in a variety of applications of nanotechnology. The goal of our current research project is to examine the photon-, electron- and hole-initiated reaction mechanisms, half-collision dynamics, and other nonequilibrium dynamics effects, occurring with excitation of adsorbates on well-characterized metal-oxide and nanocrystal surfaces. We have developed new synthesis methods for uncapped titanium oxide nanocrystals on an inert substrate with specific crystallographic orientation and controlled size distribution in a UHV STM instrument. These nanocrystals are used to evaluate nano-size effects in TiO₂ photochemistry through comparison with photochemistry on single-crystal surfaces. We use an *in situ* monochromated UV lamp to initiate photoreactions on studied surfaces or the tunneling current from the tip of our STM to excite adsorbate molecules at specific surface sites. The resulting chemistry and surface dynamics is investigated via comparison of atomic-resolution STM images of the surfaces before and after the application of excitations as well as via analysis of thermal desorption products. Additional research tools are time-of-

flight detection, standard UHV probes, XPS, and molecular computational tools, some of which are available to us through collaboration with BNL.

FY 2014 HIGHLIGHTS

Understanding the behavior of photo-generated electrical charges at the interface of the semiconductor is crucial for renewable solar-energy technologies such as photocatalysis and photovoltaics. We have explored the charge-induced phenomena on TiO₂ on a single-molecule scale using Scanning Tunneling Microscopy (STM) and temperature-programmed desorption (TPD) as a primary research tools. We have studied both single-crystal rutile(110) surface and arrays of TiO₂ nanocrystals prepared *in situ* on an Au(111) surface. Photo-induced desorption of tri-methyl acetic acid (TMAA) molecules adsorbed on TiO₂ surfaces has been selected as a model photocatalytic reaction. By using monochromated light from an Hg-Xe lamp to drive the photoreaction we demonstrated a strong dependence of the reaction rates on both the wavelength of the incident light and the state of the surface. Specifically, we have found that TMAA photodesorption rates from as-prepared rutile(110) surface for 300 nm UV light are almost 3 orders of magnitude higher than for 365 nm, in spite of the fact that photon energies for both wavelengths are well within the bandgap of titania. The difference in the photo-yields is partially explained by the different absorption depths for these two wavelengths but also by the fact that the reduced rutile(110) has a surface charge barrier that prevents the photo-generated holes with insufficient energies to interact with the adsorbed TMAA molecules. The existence of such charge barrier was demonstrated through measurements of changes in TMAA photo-desorption efficiency resulting from TiO₂ surface treatment with H₂O and O₂ prior to TMAA adsorption. Another important experimental finding was the demonstration of photocatalytic activity of Au(111)-supported TiO₂ nanocrystals for TMAA photo-desorption. The calculated efficiency of the photoreaction driven by 300 nm UV light on TiO₂ nanocrystals was comparable to that on single-crystal rutile(110) surface.

Studies of Surface Adsorbate Electronic Structure and Femtochemistry at the Fundamental Length and Time Scales

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Students:	1 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding:	\$259,000 (2014)

PROGRAM SCOPE

Our research focuses on the electronic structure and dynamics of solids, surfaces, and molecule-covered surfaces. We are interested in the surface electronic excitation and the subsequent dynamics leading to charge transfer or photochemistry. The correct description of surface electronic structure, photoexcitation, interfacial charge transfer, energy and momentum relaxation of carriers, and femtochemistry are essential for the intellectual framework for applications of photoinduced phenomena at interfaces, such as the photovoltaic and photocatalytic solar energy conversion. The research is conducted on two main themes. We are investigating the electronic structure of molecules on surfaces using low-temperature STM and electronic structure theory. In particular, we are interested in the superatom states of hollow molecules such as fullerenes and aromatic molecules. The superatom

states are interesting because they form nearly free electron bands holding the promise of metal-like charge transport in molecular systems. Furthermore, we are studying the interaction of metal-organic chains and CO₂ molecules. The capture and chemisorption of CO₂ molecules will enable molecule resolved studies of CO₂ reduction by tunneling electrons and photo excitation. The other topic concerns the fundamental electron dynamics in solid state materials and surfaces. To this end, we are studying multiphoton photoemission processes on noble metal surfaces in order to understand their phase and energy relaxation processes, as well as correlated electron, hole, phonon, etc. dynamics. Time resolved photoemission studies are extended to alkali atom and CO₂ modified noble metal surfaces with the goal of understanding their electronic structure, photo excitation processes and femtochemistry.

FY 2014 HIGHLIGHTS

We have discovered evidence for transient excitonic states in metals by multi-dimensional multi-photon photoemission spectroscopy. Such states have been predicted theoretically, but due to their short (sub-femtosecond) lifetimes, they have not been observed. In the case of Ag(111) surface, we discovered that the excitonic state formed by promotion of electron from the Shockley surface state lives for >10 fs due to inefficient screening of the Coulomb interaction. We furthermore studied the multiphoton photoemission processes on Au and Cu surfaces. In the case of these noble metals, we find evidence of photoemission, which is driven by local fields associated with the d- to sp-band transitions. In other research, we studied the electronic level alignment of the LUMO state of C₆F₆ molecule on several Cu and Au surfaces. We developed a simple theory that predicts the unoccupied state alignment based on the properties of the isolated molecule, the surface, and their main mode of interaction. The LUMO of C₆F₆ is a superatom state, which hybridizes into a nearly free electron band in molecule aggregates. We studied other superatom systems by electronic structure theory to explore the possibility of electron transport through nonnuclear media. Finally, we have described the self-catalyzed capture of CO₂ molecules by metal-organic chains on Au surfaces. Chains formed by phenylene-diisocyanide and Au atoms respond to the presence of CO₂ molecules by undergoing nanometer scale motion. Multiple chains coalesce around CO₂ molecules to capture them in single molecule wide ranks. The chemisorption of CO₂ molecules seeds the condensation of other CO₂ molecules in single molecule thick islands up to full monolayer coverage. Such condensation allows us to image CO₂ molecules by STM in the chemisorbed and physisorbed states. This system, therefore, provides a platform for studying CO₂ reduction at the single molecule scale.

EARLY CAREER: Ultrafast Electron Transport Across Nanogaps in Nanowire Circuits

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Students:	1 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	\$150,000 (2014)

PROGRAM SCOPE

In this Program we aim for a closer look at electron transfer through single molecules. To achieve this, we use ultrafast laser pulses to time stamp an electron tunneling event in a molecule that is connected between two metallic electrodes, while reading out the electron current. A key aspect of this project is the use of metallic substrates with plasmonic activity to efficiently manipulate the tunneling probability.

In the first phase of this program we developed highly sensitive tools for the ultrafast optical manipulation of tethered molecules through the evanescent surface field of plasmonic substrates. In the second phase of the program, we used these tools for exercising control over the electron tunneling probability. We have shown that electron currents across engineered nanogaps can be generated with plasmonic excitations, both in the tunneling regime and in the field emission regime.

FY 2014 HIGHLIGHTS

The highlights acquired during the period under review are as follows:

1. We have provided a firm experimental demonstration of light-controlled electron current across nanometer-sized junctions. We have shown that light-induced electron tunneling can be accomplished in nm-sized junctions in a controllable fashion. Importantly, the electron currents are stable and reproducible at ambient temperatures and pressures.
2. We have elucidated the mechanism of photo-induced electron currents across nm junctions. Electron tunneling typically occurs only in sub-nm junctions. For much larger junctions, the mechanism of field emission is prevalent. In nm-sized junctions, however, an intermediate regime exists where a transition from tunneling to field emission can be observed. We have characterized the mechanism of electron transport in this regime, and found that electron transfer is mediated both by direct tunneling through field-induced barrier lowering as well as by field emission.

A Single-Molecule Approach for Understanding and Utilizing Surface and Subsurface Absorption to Control Chemical Reactivity and Selectivity

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Funding: \$668,170 (2014-2016)

PROGRAM SCOPE

Heterogeneously catalyzed reactions are among the most scientifically intriguing and technologically important chemical conversions and play a major role in the energy, petrochemical, pharmaceutical and food industries. While the reaction pathways themselves are often highly complex, basic steps can frequently dictate important parameters like activity and selectivity. Rational design of the next generation of effective catalysts requires detailed knowledge of the molecular-level phenomena that control activity and selectivity. However, the atomic-scale structure of the active sites in industrial catalysts is hard, if not impossible, to characterize by conventional methods. We have adopted an approach using high-resolution scanning tunneling microscopy coupled with temperature programmed reaction measurements and surface spectroscopies to interrogate this chemistry. These methods offer the opportunity to study the atomic-scale composition and structure of active sites and relate this information to their ability to activate, spillover and react industrially relevant small molecules. We use these guiding principles to examine catalytic metal alloys from a new perspective and discover new processes. Specifically, we are interested in how the reactivity of a catalytically active metal is altered when it is atomically dispersed in a more inert host metal and how important reaction steps can be further tuned as a function of ensemble size, from the single atom up. Such an approach offers a means

to temper and control the reactivity of very active elements and provides fundamental design rules for cost-effective catalysts that utilize very small amounts of the precious metal.

FY 2014 HIGHLIGHTS

Co-Cu nanoparticles have recently been explored for Fischer-Tropsch synthesis (FTS) as a way to combine the long chain selectivity of Co with Cu's activity for alcohol formation in order to synthesize oxygenated transportation fuels. Depending on particle size, hydrogen dissociation can be a rate determining step in cobalt-catalyzed FTS. To understand the fundamentals of uptake and release of hydrogen from the Co/Cu bimetallic system, we prepared well-defined Co nanoparticles on Cu(111). By exploring H₂ uptake on a model catalytic system composed on Co nanoparticles deposited on Cu(111), we were able to characterize the spillover of H atoms from energetically preferred Co sites to a Cu support at catalytically relevant surface coverages of H. We show that this spillover to Cu, as well as the formation of a high-density H-(1x1) phase on Co, is facilitated by Co-Cu interface sites and that desorption from these sites occurs at a temperature that is lower than either the Cu or Co surfaces alone. Given this new low temperature pathway for H₂ uptake and release from Co-Cu interfaces, these results have ramifications for Co FTS catalysts, as it was recently demonstrated that H₂ dissociation is an important step in the rate of FTS on small Co nanoparticles. Additionally, H spillover from Co (where carbon monoxide prefers to adsorb) could limit the interface between H and CO during FTS, which could pose kinetic limitations on their reaction. This effect could be even more pronounced for the bimetallic Co-Cu catalysts currently being explored for FTS, given that segregation of the two metals has been observed in multiple systems and that CO dissociation is known to occur only on Co sites, whereas our data indicate facile spillover of H atoms to Cu sites.

Solvation Dynamics in Nanoconfined and Interfacial Liquids

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Students: 1 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding: \$99,997 (2014)

PROGRAM SCOPE

There is significant interest in nanostructured materials that can confine liquids in nanoscale pores. This is due to both the appearance of new fundamental phenomena in these systems and their wide range of potential applications, including catalysis, sensing, separations, electrochemistry, and optical materials. However, the design principles are still lacking for the development of such mesoporous (2 nm < diameter < 50 nm) materials for practical applications that take advantage of their large surface area-to-volume ratio and their high degree of tunability through pore size, shape, roughness, and chemical functionality. At the same time, this gap points to the need to improve our fundamental understanding of how complex liquid dynamics can arise from nanoscale confinement and vary strongly with the confining environment properties. In this work we are addressing some of the outstanding questions regarding nanoconfined liquid dynamics and the implications for chemical reactions by using solvation dynamics as a basis. Solvation dynamics is closely related to the reaction coordinate for charge transfer reactions such as electron or proton transfer reactions and is often dramatically affected by nanoconfinement. We are examining three key issues: 1) Solvation dynamics at silica interfaces, 2)

Origins of non-Gaussian statistics, and 3) Reorientational and hydrogen-bond dynamics of bulk and confined liquids.

FY 2014 HIGHLIGHTS

In the past year, we have used theory and simulation to advance understanding of nanoconfined liquid and hydrogen-bonding dynamics. We have worked to extend our understanding of solvation dynamics at liquid/oxide interfaces, using silica surfaces as the model. We have completed replica exchange molecular dynamics simulations of the dye molecule C153 dissolved in ethanol confined within 2.4 nm silica pores. Both ground- and excited-state C153 were simulated in hydrophilic and hydrophobic pores. Our results demonstrate that the C153 position distribution depends on its charge distribution. Moreover, the positions are determined by a subtle mixture of effects including hydrogen-bonding (H-bonding), solvent layering, and entropy. These results have implications for numerous applications as chemical processes involving charge distribution changes are ubiquitous. In collaboration with Damien Laage (Ecole Normale Supérieure, Paris), we have continued our examination of bulk and confined H-bonding liquids. First, we showed that the observed non-exponential decay for confined water reorientation that arises from individual H-bond acceptors on the pore surface each having their own timescale for exchange of H-bonding partners. The timescale for each acceptor is determined primarily by two entropic effects associated with the restrictions imposed by the pore surface on the H-bonding network. Second, we have examined the diffusion of water in nanoscale silica pores, focusing on the anisotropy and mechanism of diffusion and the role of surface heterogeneity. Third, we have simulated the linear and nonlinear infrared spectra of nanoconfined water to elucidate the information contained in different possible approaches for probing the water structure and dynamics. Fourth, we continued our work on the OH reorientation in alcohols. We have investigated how the arrangement of the same total steric bulk affects OH reorientation by looking at the four isomers of butanol.

EARLY CAREER: Imaging Interfacial Electric Fields on Ultrafast Timescales

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Students: 1 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding: \$411,000 (2014)

PROGRAM SCOPE

The objective of this research is to explore a novel methodology for visualization of ultrafast electronic processes at interfaces. The method, which is based on optical stimulation, builds upon previous success using spontaneous surface nonlinear optical probes to track the temporal evolution of interfacial electric fields resulting from charge separation across an interface. A goal is to speed signal acquisition by up to seven orders of magnitude so that laser scanning ultrafast microscopy becomes feasible. The ultimate aim is to generate movies of interfacial electronic phenomena occurring on femtosecond timescales and submicron length scales, thereby informing our understanding of disorder, heterogeneity, and morphology, and how these factors affect ensemble behavior in photovoltaic, electrochemical, and optoelectronic systems.

FY 2014 HIGHLIGHTS

In the first year of funding for this project, we successfully completed proof-of-principle demonstrations of stimulated second harmonic generation, achieving signal enhancement factors greater than 10,000. A manuscript detailing these achievements has been submitted for review, and technical improvements are under development. Additionally, we made notable progress in the synthesis of semiconductor nanocrystals, achieving unprecedented monodispersity in ensembles of PbS colloidal quantum dots (Weidman *et al.*, ACS Nano 2014), which are used in solar cells, photodetectors, and infrared imaging. Finally, supplemental funding from the CPIMS program was used to purchase a new state-of-the-art ultrafast laser system, which was installed in December, 2014. This new instrument will enable high repetition rate, multi-color pump-probe experiments with sub-20 fs time resolution.

Structural Dynamics in Complex Liquids Studied with Multidimensional Vibrational Spectroscopy

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Funding: \$271,000 (2014)

PROGRAM SCOPE

The physical properties of water and aqueous solutions are linked to the development of new sustainable energy sources. Energy conversion, storage, and transduction processes, particularly those that occur in biology and soft matter, use water for storing and moving charge. Water's physical and chemical properties depend on the ability of water molecules to participate in up to four hydrogen bonds, and the rapid fluctuations and ultrafast energy dissipation of its hydrogen-bonded networks. Our goal is a fundamental description of the properties of water at a molecular level, and how it participates in proton transport in aqueous media. Our work over the past year can be divided into four areas: (1) the generation of short pulses of broadband infrared light (BBIR) and use in two-dimensional spectroscopy (2DIR); (2) the investigation of intra- and intermolecular coupling in the vibrational relaxation process in H₂O; and (3) the study of aqueous hydroxide and strong acids to describe the interaction of the ion and water and explore the dynamics of proton transfer in water; and (4) the coupled motion of water and its hydrogen-bonding solutes. All of the experimental studies of water and aqueous solutions that we have completed in the past year have been enabled by our development of a new ultrafast infrared light source for unprecedented access to the study of dynamical intermolecular interactions. Our newest spectrometer, built since moving to the University of Chicago last year, uses a laser plasma source to generate coherent pulses of broadband infrared light shorter than 70 fs and have a spectrum spanning the entire mid-IR, from 3800 cm⁻¹ to <1000 cm⁻¹. This source is integrated as a probe pulse in ultrafast pump-probe and 2DIR experiments. Our development of this spectrometer continues and future plans involve amplification of this source to use for excitation and detection in 2DIR experiments.

FY 2014 HIGHLIGHTS

The large bandwidth of our BBIR probe pulse has helped us study the broad absorption features in neat H₂O. The most striking feature we observed in the broadband 2DIR and transient absorption spectra of

H₂O is the broad excited state absorption between the $v=1$ and $v=2$ states of the OH stretch, which is over 1000 cm⁻¹ broad and relaxes with a 275 fs time constant. Ongoing work is aimed at theoretically modeling the collective vibrational dynamics of H₂O. Focusing on our long-term objective to characterize the structure and transport of excess protons in water, we have performed BB 2DIR spectroscopy of aqueous strong acids. Like hydroxide solutions, excess protons in water give rise to a continuum absorption in the mid-IR that is largely featureless and spans over 2000 cm⁻¹. 2DIR spectroscopy reveals that the entire continuum responds immediately upon exciting OH stretching vibrations and continuum relaxation occurs on sub-100 fs timescales. Our ongoing work is aimed at studying spectral regions associated with Eigen complexes, improving vibrational assignments to features within the continuum, and using excitation and probing throughout the IR to follow the ultrafast exchange of proton structures. Finally, to understand the 2D IR spectroscopic signatures of a model hydrogen-bonding interaction, we performed BB 2DIR experiments to watch the correlated vibrational motion of the hydrogen bond donor and acceptor. We used dimers of N-methylacetamide, in which the N-H group donates a hydrogen bond to the C=O group of another molecule. We identified a series of crosspeaks that arise solely from the intermolecular interaction, and demonstrated that the N-H C=O and C-N bonds on both partners move synchronously as a result of the hydrogen bond. These results are being extended to water-solute systems, where the water forms a hydrogen bond with the solute.

The Role of Electronic Excitations on Chemical Reaction Dynamics at Metal, Semiconductor, and Nanoparticle Surfaces

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

Achieving enhanced control of the rates and molecular pathways of chemical reactions at the surfaces of metals, semiconductors and nanoparticles will have impact in many fields of science and engineering, including heterogeneous catalysis, photocatalysis, materials processing, corrosion, solar energy conversion and nanoscience. However, our current atomic-level understanding of chemical reactions at surfaces is incomplete and flawed. Conventional theories of chemical dynamics are based on the Born-Oppenheimer separation of electronic and nuclear motion. Even when describing dynamics at metal surfaces where it has long been recognized that the Born-Oppenheimer approximation is not valid, the conventional approach is still used, perhaps patched up by introducing friction to account for electron-hole pair excitations or curve crossings to account for electron transfer. There is growing experimental evidence that this is not adequate. We are examining the influence of electronic transitions on chemical reaction dynamics at metal and semiconductor surfaces. Our program includes the development of new theoretical and computational methods for nonadiabatic dynamics at surfaces, as well as the application of these methods to specific chemical systems of experimental attention. Our objective is not only to advance our ability to simulate experiments quantitatively, but also to construct the theoretical framework for understanding the underlying factors that govern molecular motion at surfaces and to aid in the conception of new experiments that most directly probe the critical issues.

FY 2014 HIGHLIGHTS

Two major highlights emerged from our laboratory in Fiscal Year 2014. First, we have completed a thorough testing of our Independent Electron Surface Hopping theory on NO scattering from Au(111) in which the N–O stretching coordinate is treated by quantum mechanics. This is the first attempt of which we are aware to combine quantum mechanical electronic and vibrational transitions on an equal footing by surface hopping. The calculations are computationally feasible, and the classical and quantum results for state-to-state vibrational excitation of scattering of NO ($v=0$) are in surprisingly good accord with each other and with experiment. Second, we have developed a theoretical model that convincingly explains some remarkable recent measurements by Guo and Yan (Yale University) of the thermal rate of isomerization of the 11-cis retinyl chromophore in the visual pigment rhodopsin: at temperatures between 52.0 and 64.6°C, the measured rate constants fit well to an Arrhenius straight line with, however, an unexpectedly large activation energy of 114 ± 8 kcal/mol and an unprecedentedly large prefactor of 1072 ± 5 s⁻¹, about 45 orders of magnitude larger than any previously reported prefactor for a unimolecular reaction! A key factor of the model is the lowering of the reaction barrier when the protein is melted compared to when the chromophore is more constrained in the rigid folded state. If the initial state is ordered and the transition state is partially or completely melted, there will be huge increases in both the enthalpy and entropy of activation, as observed. This behavior may well prove to be quite general, not only in biological reactions, but also in condensed phase and surface reactions carried out at temperatures and pressures close to 2D or 3D phase transitions. (Collaborative: Experiments by Ying and Guo, theory by Tully).

Room Temperature Single-Molecule Detection and Imaging by Stimulated Raman Scattering Microscopy

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

The objective of this proposal is to achieve Raman-based single-molecule detection using near-resonant stimulated Raman scattering (SRS) microscopy. SRS microscopy was a new optical technique that was developed in our lab a few years ago for imaging heterogeneous samples based on their intrinsic vibrational contrasts, which provides much higher molecular specificity than absorption and fluorescence. It has improved the imaging speed over traditional confocal Raman imaging by a few orders of magnitude. However, the sensitivity limit of SRS microscopy is still confined to the millimolar range, similar to confocal Raman. We propose to capitalize on our state-of-the-art SRS microscopy and develop near-resonance enhanced SRS for sensitivity enhancement with the ultimate goal of achieving single molecule detection.

FY 2014 HIGHLIGHTS

In the last funding period, we have achieved a SRS detection sensitivity limit of 100nM for beta-carotene, a factor of ten away from single molecule detection. This is done through the use of near-resonant SRS by pumping at 532nm. The bottleneck of further improvement in sensitivity is

photodamage: the beta-carotene molecule is destroyed before enough photons can be collected. To overcome this problem, we designed a new molecule based on the principle of triplet state quenching that is recently employed to improve the photostability of fluorophores. We have successfully synthesized a beta-carotene molecule covalently conjugated to a triplet state quencher molecule cyclooctatetraene. However, compared with beta-carotene, the synthesized molecule does not show improved photostability when excited with 532nm and 578nm picosecond lasers. We are still investigating the possible origin of photodamage and developing alternative routes to stabilize the carotenoid molecule under near-resonant excitation. A major development that results from this process is our development of frequency-modulation SRS imaging technique. Although SRS imaging has a major advantage compared to CARS in that it automatically removes non-resonant background, it is still susceptible to cross-phase modulation (XPM) induced background when the SRS signal is extremely weak. XPM-induced background is mostly independent of the pump and probe wavelengths, and therefore can be removed by subtracting on-resonance and off-resonance SRS signal. We termed this technique frequency-modulation SRS. Based on a previously demonstrated femtosecond spectral focusing SRS technique, we have successfully demonstrated frequency-modulation SRS by rapidly switching the time delay between the pump and probe pulses at 20 MHz. Because in spectral focusing SRS, the probed Raman frequency depends linear on the time delay, XPM-induced background is effectively removed in real-time by up to 10 fold.

DOE National Laboratories

Molecular Environmental Sciences (MES) Beamline

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Hendrik Bluhm; Lawrence Berkeley National Laboratory
Mary Gilles; Lawrence Berkeley National Laboratory
Students: 2 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding: \$873,000 (2014)

PROGRAM SCOPE

The LBNL Chemical Sciences Division (CSD) Molecular Environmental Sciences (MES) Beamline at the Advanced Light Source (ALS) is a leading national resource in the field of soft X-ray synchrotron radiation research. It supports multidisciplinary, state-of-the-art spatially-resolved, molecular-level spectroscopic investigations of the chemistry and physics at complex interfaces under increasingly real environments by utilizing revolutionary new, best-in class experimental resources for staff and users. The MES Beamline and staff carry out and make possible unique, forefront molecular-level research in catalysis, nanoscience, contemporary surface science, f-element chemistry, aerosol science, environmental science, and atomic, molecular, and optical science that contribute knowledge necessary for the U.S. DOE to successfully address its energy mission. The MES program develops and implements innovative, world-leading scanning transmission X-ray microscope (STXM) and ambient pressure photoelectron spectroscopy (APPES) instrumentation. Research at the MES Beamline and by staff are providing some of the first significant molecular-level understandings of important chemical and physical processes taking place at interfaces under real or more realistic conditions than ever before possible for scientific disciplines directly-related to energy. The scientific programs of the MES Beamline are synergistic with

those of international, national, and local beamline facilities including the LBNL CSD Chemical Dynamics Beamline Facility at the ALS.

FY 2014 HIGHLIGHTS

The interaction of carbon monoxide with surfaces and interfaces (metal, metal alloy and 2D film interface) was mapped out from pristine ultra-high vacuum to ambient conditions with X-ray photoelectron spectroscopy. New evidence for 5f covalency in actinocenes was determined from Carbon K-Edge X-Ray Absorption spectroscopy when combined with electronic structure theory. A novel experimental platform was implemented which allowed for *In Situ* Soft X-Ray Absorption Spectroscopy of Flames. Absorbance images for methane, carbon monoxide and carbon dioxide were measured at the carbon K edge by raster scanning a flame burner across the X-Ray beam. The surface active species in substituted Lanthanum Iron Perovskite-Oxide Electrocatalysts were observed in an *In-Operando* system. The interfacial photoelectrochemical dynamics in dye sensitized solar cells were captured with picosecond time-Resolved X-Ray photoelectron spectroscopy by combining ambient pressure photoemission spectroscopy with tunable X-Ray radiation and a high repetition rate laser synchronized to the Advanced Light Source. Novel developments in instrumentation and computer algorithms led to chemical composition mapping with nanometer resolution by Soft X-Ray Microscopy. Selective Gas Adsorption in the presence of water on hybrid nanoporous films was measured via ambient pressure photoemission spectroscopy. Spectrochemical imaging of aerosol aging and brown carbon chromophores was performed with scanning X-Ray transmission microscopy.

Kinetics of Charge Transfer in a Heterogeneous Catalyst-Reactant System

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Funding: \$320,000 (2014)

PROGRAM SCOPE

One of the greatest challenges in the design of efficient and selective catalysis technologies is the limited fundamental understanding of how interfacial properties at solid state/reactant interfaces guide catalytic reactions. What is needed is to directly follow the trajectory of how charge carriers in solid state catalysts initiate interfacial charge capture by reactant molecules, from the creation of the charge carrier in the bulk, to its accumulation at the interface, and to the moment at which a reactant molecule transforms and, in the process, consumes the charge carrier. This proposal will use optical and infrared pump-probe spectroscopy, inclusive of second harmonic generation, transient diffraction gratings, and sum frequency generation to investigate the kinetics of charge transfer at a catalyst/reactant interface. The charges will be injected into the catalyst via an embedded photovoltaic or Schottky junction and the reactant environment will be controlled in a vacuum chamber. Oxidative reactions are chosen since they are strongly endoergic and often the limiting factor in full integrated artificial photosynthetic systems. Methanol oxidation and water oxidation will be explored on three different types of oxides (n-type TiO₂, p-type Co₃O₄, and RuO₂). Ferrocene oxidation will be used as a model one electron transfer reaction.

FY 2014 HIGHLIGHTS

New transient reflectance results on n-SrTiO₃ in an in-situ electrochemical cell reveal a marked change in kinetics as a function of voltage applied on the electrochemical cell. In a recently published manuscript, we ascribe the potential dependent hole kinetics to mapping out the activation barrier of the initial hole transfer of the water oxidation reaction, [h⁺] + [OH⁻] to form [OH], where OH is a neutral, OH radical. In particular, we quantify how much a change in the potential of interfacial holes reduces the activation barrier. We also find the kinetics of charge transfer at the equilibrium thermodynamic potential of the reaction. The values are within expectations for a simple, one hole transfer reaction, as can be determined by electrochemistry for such reactions using steady state current flow. Steady state current, however, cannot follow multi-component reactions accurately and without extensive modeling. The new finding here is that we have been able to both separately follow and quantify a single hole transfer step from a multi hole transfer reaction using transient spectroscopy. The physical picture is that we have quantified the initial step to transferring a hole over from a delocalized valence band edge of O 2p orbitals in the solid state catalyst into a molecular oxygen bond at the interface.

Ultrafast Molecular Scale Chemical Imaging

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Funding: \$542,000 (2014)

PROGRAM SCOPE

Photophysical processes at the heart of photovoltaic, photocatalytic and photosynthetic processes in molecular-scale complexes hinge on structure-property relationships that are enshrined at the atomic scale, far beyond the spatial resolution of optical spectroscopies alone. The goal of this project is to develop and exploit an advanced experimental approach that integrates ultra-high vacuum (UHV) scanning tunneling microscopy and spectroscopy (STM/STS) and single particle laser spectroscopy in order to explore the photophysics of single molecules or molecular systems with atomic-scale spatial resolution and ultrafast time scales. The overarching scientific goal of this work is to experimentally decipher the correlation between the photophysical functioning of a molecular system and its detailed conformation and local environment; this would provide a critical touchstone for connecting with theory to develop a fundamental understanding of these processes. We are targeting transport and photophysical processes in (i) self-assembled small molecule acceptor-donor complexes, (ii) covalently-bonded acceptor-donor molecules, and (iii) bio-inspired photosynthetic molecular systems deposited and probed on UHV clean surfaces. In addition to metal substrates, we are also exploring 2D materials (e.g. graphene) as a substrate to provide a weakly-interacting surface in order to minimize perturbations to the electronic and optical properties of the molecular systems. After developing an understanding of morphology and electronic structure of the molecular systems on these surfaces with UHV STM, we will explore photoexcitation and photo-induced charge separation in these well-characterized systems using single particle laser excitation and spectroscopy techniques.

FY 2014 HIGHLIGHTS

We have been building on recent successes in our project involving the investigation of self-assembled chiral donor-acceptor heterojunctions on Cu(111), the demonstration of the weak coupling of donor and acceptor molecules to a graphene substrate, and the growth of graphene on Ag(111). Laser excitation and spectroscopy of these systems requires custom UHV STM instrumentation developed in house; we have recently improved the energy resolution and stability for these measurements with the demonstration of our homebuilt low temperature (4K) UHV STM with integrated optical microscopy and spectroscopy access. In order to limit the mobility of molecules on graphene systems, we have developed a method in which molecules are deposited onto a pre-formed network of surface supported graphene nanoribbons. We used this method to localize metalized porphyrin molecules, TBrPP-Co, on nanoribbons of various widths. This enabled us to spectroscopically study the molecules, where a feature characteristic of the magnetic 'Kondo' interaction was observed. These results are the first indication of a hetero-molecular Kondo interaction through any graphene system. Beyond graphene (2D carbon), we have been exploring other 2D materials to serve as substrates for our experiments and ultimately as platforms for molecular electronics, opto-electronics, and photovoltaics. The ability to reduce silicon to a single atomically thin layer ("silicene") has received considerable attention. However, its realization remains elusive. Despite previous reports of the growth and observation of "silicene" on an Ag(111) surface by several research groups, we have demonstrated that the observed structure was most likely a previously known Ag surface reconstruction forming on bulk silicon precipitation. This result underscores the challenges associated with understanding structure at the atomic scale and its critical role in understanding behavior and developing applications.

Chemical Kinetics and Dynamics at Interfaces

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Funding: \$3,271,000 (2014)

PROGRAM SCOPE

The Condensed Phase Chemical Physics Program supports the mission of the DOE Office of Basic Energy Sciences to foster and support fundamental research in the natural sciences to provide a basis for new and improved energy technologies (e.g., catalysis and energy conversion) and for understanding and mitigating the environmental impacts of energy use. This research provides a foundation for understanding fundamental interactions of atoms, molecules, and ions with materials and with photons and electrons in their chemical environment. Research underpins the fundamental knowledge of chemical transport and reactivity in the condensed phase. It also addresses fundamental uncertainties in thermal and non-thermal (i.e., radiation) chemistry, interfacial molecular and ionic transport (key to subsurface contaminant transport and to separations processes) and other processes in complex

systems related to energy use, environmental remediation, and waste management. Our research focuses on structures and processes of molecular and nanoscale systems in complex environments such as condensed phases and interfaces. Experimental and theoretical models are used to better understand natural systems and guide the development of new materials and approaches for clean and efficient energy use. Another central feature is the development of new experimental methods with broad applications to research in the natural sciences.

FY 2014 HIGHLIGHTS

Research highlights in FY 2014 include (1) the investigation of the competitive displacement kinetics between H₂O and CO₂ on model oxide (TiO₂ (110)) and natural mineral (Mg₂SiO₄(011), forsterite) surfaces using temperature desorption and molecular beam techniques; (2) the demonstration of depth dependent radiation chemistry in electron-irradiated H₂O/CO/H₂O ices where it was discovered that the product distribution is dependent on the position of the CO layer in the H₂O ice film; (3) the report that the Cl⁻-H₃O⁺ contact ion pair persists throughout a broad concentration range and that characterizing distinct populations of these ion pairs gives rise to a novel molecular level description of how to view the reaction network for acid dissociation and how it relates to our fundamental picture of acid–base equilibria; (4) the publication of a high resolution negative ion photoelectron spectrum of a model green fluorescent protein, GFP, chromophore anion, that produced experimental adiabatic and vertical detachment energies with sufficient accuracy and resolution to provide much needed robust benchmarks for future theoretical investigations; (5) the demonstration of how the efficiency of coupling light waves into isolated plasmonic holes can be tuned by varying hole diameter and how efficient optical coupling and nanohole assemblies can be used to rationally control plasmon propagation and interferometric plasmonic lensing.

Surface Chemical Dynamics

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Funding: \$1,070,000 (2014)

PROGRAM SCOPE

This program focuses on fundamental investigations of the dynamics, energetics and morphology-dependence of thermal and photoinduced reactions on planar and nanostructured surfaces that play key roles in energy-related catalysis and photocatalysis. Laser pump-probe methods are used to investigate the dynamics of interfacial charge and energy transfer that lead to adsorbate reaction on metal and metal oxide surfaces. State- and energy-resolved measurements of the gas-phase products are used to infer the dynamics of product formation and desorption. Time-resolved correlation techniques follow surface reactions in real time and are used to infer the dynamics of adsorbate–substrate energy transfer. Measurement of the interfacial electronic structure is used to investigate the impact of adsorbate-surface and cluster-support interactions on the activity of thermal and photoinduced reactions. Capabilities to synthesize and investigate the surface chemical dynamics of arrays of supported metal nanoparticles (NPs) on oxide surfaces include the deposition of size-selected

gas-phase clusters as well as solution-phase synthesis and deposition of narrow-size-distribution nanometer-scale particles.

FY 2014 HIGHLIGHTS

- We are using nanoparticle (NP) arrays to investigate the size-dependence of the surface reaction dynamics in ultrafast time-resolved studies. Recent advances in our diblock-copolymer inverse-micelle-based synthesis of palladium nanoparticle arrays on titanium dioxide have provided good size control in the few-nm size range. We are now able to tune the mean particle size between 3 and 8 nm, while maintaining an interparticle distance of approximately 35 nm.
- We have extended earlier surface dynamics investigations on single crystal Pd(111). We recently observed a dramatic coverage dependence in the photoinduced desorption cross section for CO from Pd(111) that correlates with population of atop binding sites. We also found that the presence of O⁻ atoms further enhances this cross section. Understanding binding-site and lateral-interaction effects is crucial to the interpretation of NP measurements.
- Velocity map imaging (VMI) in conjunction with a novel 4D fast camera (x, y, time, intensity) have been used for the first time to discriminate between primary and secondary products from surface photoreactions. Initial experiments concerned the fate of ethyl radicals resulting from the UV photooxidation of 2-butanone on TiO₂(110), which previous studies suggest undergo secondary reactions to form ethane and ethylene. The VMI images, however, prove that all the observed product ions originate from the nascent ethyl radical. This proof-of-principle experiment demonstrates the utility of coupling VMI and 4D imaging for unraveling the product distributions from photoreactions at surfaces.
- Two-photon photoemission has been used to probe the interfacial electronic structure of a wide range of metal oxide nanoclusters (M_xO_y; M = W, Mo, Ti, Nb) supported on Cu(111) and Cu₂O/Cu(111) surfaces.

Condensed Phase and Interfacial Molecular Science

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Phillip Geissler; Lawrence Berkeley National Laboratory
Charles B. Harris; Lawrence Berkeley National Laboratory
Richard Saykally; Lawrence Berkeley National Laboratory
Students: 2 Postdoctoral Fellow(s), 9 Graduate(s), 0 Undergraduate(s)
Funding: \$1,193,000 (2014)

PROGRAM SCOPE

Condensed Phase and Interfacial Molecular Science (CPIMS) research seeks a molecular-level understanding of chemical, physical, and electron-driven processes in aqueous media and at interfaces, as these underlie contemporary directions in energy production and storage, and their environmental consequences. Studies of model condensed-phase systems target first-principles understanding of molecular reactivity and dynamical processes in solution and at interfaces by confronting the transition from molecular-scale chemistry to collective phenomena in complex systems. Novel theory and

experiments address the details of solvation (particularly hydration) and interfacial properties and dynamics of a variety of energy related phenomena, such as the selective surface adsorption of ions and the development of models to describe molecular details of evaporation (currently one of the principal uncertainties in modeling the long-term effects of fossil fuel by products) and free radical reactions of hydrocarbons at aqueous interfaces. New models are developed for examining spatial distributions of ions and complex organic molecules near interfaces and the nature of molecular vibrations in nonuniform liquid systems. Complementary theory and experiments address charge transport at complex interfaces and the effects of phase transitions on charge transport, with the goal of advancing battery, fuel cell, and solar fuel production technology.

FY 2014 HIGHLIGHTS

Recent advances in understanding liquid interfacial dynamics include a general and efficient procedure for identifying instantaneous interfaces from molecular coordinates and a generalization of umbrella sampling methods for collecting statistics on rare but important density fluctuations. These methods have identified important mechanistic pathways in water evaporation, the structure and dynamics of water at metal and hydrophobic interfaces. New theoretical descriptions have been developed of selective ion adsorption at the air-water interface through the construction of an analytically tractable microscopic model for ion solvation, yielding further insights into the molecular underpinnings of anion adsorption selectivity at the liquid interface. The dissolution of carbon dioxide in water and the ensuing hydrolysis reactions are of profound importance for understanding the behavior and control of carbon in the terrestrial environment. New experiments at the Advanced Light Source measured the first X-ray absorption spectra of aqueous carbonates, including the short-lived carbonic acid species itself. Measured and calculated spectra are in excellent agreement and reveal that each carbonate species exhibits similar, but distinct, spectral features which are interpreted in terms of the relative C-O bond strengths, molecular configuration, and hydration strength. Recent progress has been made understanding the excess electron dynamics in ultrathin layers of NaCl on Ag(100); a model system for a wide range of technologically relevant devices. It was observed that the free electrons excited into the image potential states localize on the ultrafast time scale due to trapping at neutral defect states existing at the NaCl/vacuum interface. These observed trap states could have a potential impact on electron transport in systems where ultrathin layers of insulating layers are used, and have a subsequent impact on device efficiency.

EARLY CAREER: Free Radical Reactions Hydrocarbon at Aqueous Interfaces

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Funding: \$500,000 (2014)

PROGRAM SCOPE

Chemical reactions of hydrocarbon radicals occurring at water and electrolyte interfaces govern a wide array of environmentally and technologically important processes in electrochemistry, catalysis, aerosol aging, cloud chemistry, lipid peroxidation, and corrosion. Predictions of interfacial reactivity based solely upon chemical structure (e.g. the number and kind of molecular reactive sites in an isolated gas phase

molecule) are often inaccurate by many orders of magnitude, since interfacial molecular orientation and solvent structure all play significant and complex roles in controlling the activation energy of a surface reaction. This proposed research program will combine state-of-the-art ambient pressure droplet train X-ray photoelectron spectroscopy with novel surface sensitive mass spectrometry to reveal how chemical structure, thermodynamic phase, interfacial thickness and solvent structure govern molecular weight growth and degradation of hydrocarbons at water and electrolyte interfaces. This work supports key missions of the DOE Basic Energy Sciences program to better assess, mitigate and control the environmental impacts of energy use by providing innovative approaches for obtaining a first principles understanding of surface chemistry of aqueous interfaces.

FY 2014 HIGHLIGHTS

Sensitive measurements of the droplet size were conducted, at a relative humidity (~99.9%) just below saturation, on submicron particles containing an ammonium sulfate core and an organic layer of a model compound of varying thickness. The 12 model organic compounds are a series of di-carboxylic acids (C_3 to C_{10}), cis-pinonic, oleic, lauric, and myristic acids, which represent a broad range in solubility from miscible (malonic acid) to insoluble. The growth in droplet size with increasing organic fraction cannot be explained by assuming the organic material is dissolved in the bulk droplet. Instead, the wet droplet diameters exhibit a complex and non-linear dependence on organic volume fraction, leading to droplet growth that is in some cases smaller and in others larger than that predicted by bulk solubility alone. A model based on the two-dimensional van der Waals equation of state is used to explain the complex droplet growth with organic aerosol fraction and dry diameter. The model suggests that mono- and di-carboxylic acids with limited water solubility partition to the droplet interface and reduce surface tension only after a two dimensional (2D) condensed monolayer is formed. There is a clear alternation in the threshold for droplet growth observed for odd and even carbon numbered diacids, explained in the model by differences in the excluded molecular areas of even and odd diacids. These differences are consistent with the odd diacids being arranged at the droplet interface in end-to-end configurations with only one acid group in contact with the aqueous phase; in contrast to even carbon numbered diacids forming folded films with both acids groups in contact with the bulk phase. These results reveal a new and complex relationship between the composition of an organic particle and its water uptake, suggesting that organic surface films might strongly influence the multiphase surface chemistry of organic particles as well as cloud droplet formation.

Gas Phase Chemical Physics

Institutions Receiving Grants

Theoretical Investigation of Kinetic Processes in Small Radicals

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Funding: \$155,811 (2014)

PROGRAM SCOPE

Our group studies inelastic and reactive collisions of small molecules, focusing on radicals important in combustion environments. Our goal is the better understanding of kinetic processes that may be difficult to access experimentally. An essential component is the accurate determination of potential energy surfaces (PESs). After fitting the *ab initio* points to obtain global PESs, we treat the dynamics using time-independent (close-coupling) methods. A focus of recent work in our program has been the study of energy transfer collisions (rotationally, vibrationally, and/or electronically inelastic) of small hydrocarbon radicals (CH_2 and CH_3). Our calculations have been compared with experimental measurements of rate constants (CH_2) and differential cross sections (CH_3). We have also initiated the calculation of accurate transport properties for collision systems involving a free radical, concentrating on collision pairs relevant to species in a $\text{H}_2/\text{O}_2/\text{He}$ flame. We are presently using these accurate transport properties in 1-dimensional flame simulations.

FY 2014 HIGHLIGHTS

We have extended study of collisional relaxation of methylene (CH_2) to the vibrational relaxation of the bending mode of $\text{CH}_2(\text{X})$ in collisions with He. A characteristic of A to X collision-induced internal conversion (CIIC), of methylene is the dominant role of weak coupling between perturbed pairs of rotational levels. We have computed CIIC rate constants with a model involving coherent mixing of the scattering T-matrix elements associated with collisional transitions within the unmixed X and a states. We have used these rate constants to simulate the relaxation of $\text{CH}_2(\text{X},a)$ in collisions with He. The group of Orr-Ewing (Bristol, UK) has measured differential cross sections for scattering of CD_3 with He, H_2 , Ar, and N_2 . We have employed PES's determined by our group for the first 3 collision partners to compute differential cross sections. We find excellent agreement between the measurements and our calculations. We find that the dynamics of collision of the symmetric top CD_3 is richer than that of a diatomic. Chemical kinetic models require knowledge of not only the rate constants of all the relevant species, but also transport properties for an accurate description of the species concentrations, as well as for the calculation of flame. We have been computing accurate transport properties for a series of collision systems involving a free radical. In current work, we computed transport properties for collision pairs relevant to species in species in a $\text{H}_2/\text{O}_2/\text{He}$ flame, with the use of *ab initio* PES's. We have carried 1-dimensional flame simulations of a freely propagating $\text{H}_2/\text{O}_2/\text{He}$ flame with two sets of transport properties. The first set employed transport properties obtained with the conventional method of parameterized LJ 12-6 potentials, while in the second set transport properties for the above collision

pairs were substituted. A modest increase in laminar flame speeds, comparable to differences for various chemistry models, was found for both flames.

Predictive Large-Eddy Simulation of Supercritical pressure Reactive Flows in the Cold-Ignition Regime

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Funding: \$405,000 (2014-2017)

PROGRAM SCOPE

We address issues highlighted in the Basic Energy Needs for Clean and Efficient Combustion of 21st Century Transportation Fuels (DOE BES, 2006) under the topic of Combustion under Extreme Pressure. Specifically: (1) “the most basic concepts of thermal autoignition” are “based on experience and theory at near atmospheric pressures” and that “as pressure increases significantly..., many of these conceptual pictures begin to change or disappear” (2) “A better description of the coupling and interaction of high pressure flow and molecular transport processes with chemistry is also necessary”, (3) “Ignition and flame propagation of alternative and renewable fuels, as well as of the changing feed stocks of conventional fossil-based fuels, are very likely to be much different at very high pressures than under the more familiar, lower pressure conditions of current engines.” (4) “Under such conditions distinctions between gas and liquid phases become moot, new equations of state must be used...”, (5) There must be “a re-examination of the basic assumptions that govern the physics and chemistry related to combustion; and the need for this type of re-examination increases as the combustion pressure increases.” Under “Multiscale Modeling” it is stated “The combination of unexplored thermodynamic environments and new physical and chemical fuel properties results in complex interactions among multiphase (according to the above, the multiphase distinction becomes moot with increasing pressure) fluid dynamics, thermodynamic properties, heat transfer, and chemical kinetics that are not understood even at a fundamental level.” The objective of this study is the investigation of the coupling among thermodynamics, transport properties, intrinsic kinetics and turbulence under the high-pressure and the relatively (with respect to combustion) low-temperature conditions of the auto-ignition regime, with particular emphasis on the manifestation of this coupling on the effective kinetic rate.

FY 2014 HIGHLIGHTS

To accomplish the goals we have created a database of several Direct Numerical Simulations of a reactive temporal mixing layer created between two counter-flow streams: air mixed with traces of water and carbon dioxide in the upper stream at 1000 K temperature and n-heptane with traces of water and carbon dioxide in the lower stream at 600 K temperature. The water and carbon dioxide mimic exhaust gas recirculation. The initial Reynolds number, the free-stream pressure (60 – 80 bar) and the amounts of water and carbon dioxide were varied among simulations. This database is currently being thoroughly analyzed to understand the peculiarities of the turbulent reaction at high pressure. The analysis conducted so far has revealed that (1) the reaction zone is a combination of a diffusion flame flanked by two premixed flames, (2) due to occurring uphill diffusion of water and carbon dioxide at the high pressures under consideration, exhaust gas recirculation has the advantage of increasing turbulence through the formation of high species-density-gradient regions which act akin to a mesh in

the flow, and (3) the highest dissipation is that due to the reaction, but viscous, species-mass and heat dissipation may be active at other locations, meaning that all these various contributions to the dissipation should be modeled in Large Eddy Simulation.

EARLY CAREER: Towards Predictive Simulations of Soot Formation: From Surrogate to Turbulence

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Funding: \$159,733 (2014)

PROGRAM SCOPE

The combustion of hydrocarbon fuels, including kerosene, gasoline, and diesel, leads to the formation of soot particles which are known to be the source of several health problems and environmental issues. The objective of the proposed work is to fill the gap in the present understanding and modeling of soot formation both in laminar and turbulent flames. This effort spans all critical length scales from the molecular level to large scale turbulent transport. The objectives are three fold: 1) develop the first combined chemical and soot model validated for all relevant components usually found in real fuel surrogates; 2) develop a framework able to explain the complete evolution of soot particles from cluster of PAHs to oxidation of large fractal aggregates; 3) understand and model the interplay between unsteady chemistry, differential diffusion, and turbulent transport. While this project focuses on numerical simulations, the objective is also to develop a true synergy between experiments and computations through collaborations with experimental groups for each topic.

FY 2014 HIGHLIGHTS

In the past year, we applied our latest developments in the simulations of multiple laminar premixed flames, laminar co-flow diffusion flames, and turbulent jet diffusion flames. Central to this effort, Large Eddy Simulations (LES) have been performed on an ethylene/air piloted turbulent non-premixed sooting jet flame to quantify the importance of aromatic chemistry-turbulence interactions. Aromatic species are of primary importance since their concentrations control directly the soot nucleation rates. The proposed simulation framework relies on four major components: a gas-phase chemistry model, a turbulence closure model, a PAH relaxation model, and finally a soot model. The results, in excellent agreement with experimental data from Sandia National Laboratory, highlight the greater importance of unsteady aromatic-chemistry over the most commonly assumed soot-turbulence interactions. Consistently with our results in the laminar premixed and diffusion flames, these turbulent flame results also emphasize the need for a more fundamental understanding of the growth of aromatic molecules and their nucleation into soot particles. Work has also been done on these last two aspects. For instance, we showed that excited states of PAH molecules might play a critical role in the rate and reversibility of the soot inception process. The year 2014 culminated with the second International Sooting Flames (ISF) workshop where our work was showcased.

Dynamics of Product Branching in Elementary Combustion Reactions - OH + Alkenes and Nitrogen

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Funding: \$163,000 (2014)

PROGRAM SCOPE

Radical intermediates play a key role in combustion. The addition of a radical such as OH to an unsaturated hydrocarbon generates a transient, highly vibrationally excited, radical intermediate along the bimolecular reaction coordinate. Our experiments directly investigate the dynamics of the product channels that arise from such radical intermediates. The experiments developed in my group generate a particular isomeric form of an unstable radical intermediate and study the branching between the ensuing product channels of the energized radical as a function of its internal rotational and vibrational energy under collision-less conditions. The experiments use a combination of: 1) measurement of product velocity and angular distributions in a crossed laser-molecular beam apparatus, with electron bombardment detection in my lab in Chicago or 2) with tunable vacuum ultraviolet photoionization at Taiwan's National Synchrotron Radiation Research Center (NSRRC), and 3) velocity map imaging using state-selective REMPI ionization, single photon ionization, and now tunable vacuum ultraviolet photoionization of radical intermediates and reaction products.

FY 2014 HIGHLIGHTS

This year we finished and published our experiments on two radical intermediates in the reaction of OH + propene, the 1-hydroxy-2-propyl radical produced when the OH adds to an end carbon and the 2-hydroxy-1-propyl radical from addition at the center carbon. Using a combination of velocity map imaging and photofragment translational spectroscopy, we detected several products from the unimolecular dissociation of the radical intermediates, including OH + propene, methyl + acetaldehyde, and ethyl + formaldehyde. Using a velocity map imaging apparatus, we produced the radical intermediates photolytically from brominated precursors, which allowed us to determine the internal energy distribution of the radical intermediate from the speed distribution of the recoiling bromine atoms. Resolving the velocity distribution of $\text{Br}(^2P_{1/2})$ and $\text{Br}(^2P_{3/2})$ separately allows us to determine the total (vibrational + rotational) internal energy distribution in the nascent radicals. By modeling the amount of rotational energy imparted to the radicals upon dissociation of the halogenated precursors, we determine the vibrational energy distribution of the nascent radicals. With this model, we predict the percentage of radicals having vibrational energy above and below the lowest dissociation barrier, that to OH + propene; it accurately predicts the measured velocity distribution of stable radicals. We also use the angular momenta of the unstable radicals to estimate the energy partitioned to relative kinetic energy when they dissociate to OH + propene radicals. The results develop insight on product channel branching in reactions that proceed via an addition/elimination mechanism and provide a key benchmark for emerging electronic structure and dynamics calculations on polyatomic reactions that proceed through unstable radical intermediates.

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Funding: \$350,000 (2014-2016)

PROGRAM SCOPE

This research program focuses on studies of the energetics and reaction dynamics of transient neutral molecules and collision complexes relevant to combustion phenomena. The general goal is to carry out benchmark-quality measurements of radicals and neutral reaction systems including oxygenated radicals and hydroxyl radical reactions. Measurements of energetics, including bond dissociation energies, tunneling dissociation rates and product branching ratios for oxygenated radicals and hydroxyl radical reactions have been a central focus of recent work. An important element of this program has included close collaboration with theoretical groups to test *ab initio* potential energy surfaces and quantum dynamics calculations that will be required for first-principles understanding of more complex chemical systems. The experiments use photodetachment of precursor molecular and cluster anions to prepare energy-selected reactive intermediates, and then directly measure the stability and dissociation dynamics of energy-selected reactive intermediates. These experiments combine photoelectron spectroscopy with photofragment translational spectroscopy in the unique technique called photoelectron-photofragment coincidence (PPC) spectroscopy for studying dissociative photodetachment (DPD) processes. The PPC technique now makes use of an electrostatic ion beam trap (EIBT), permitting the storage of molecular anions for many seconds and also opening the door to preparation of vibrationally excited anions for studying new aspects of chemical reactivity. A next generation improvement of this apparatus involving a new ion source, and a cryogenic octupole accumulator trap to improve preparation of larger molecular systems with very low internal temperatures is in progress, and will allow studies of larger species relevant to biofuel combustion under well-defined conditions.

FY 2014 HIGHLIGHTS

The fluorine-water system was studied using the DPD of the fluoride-water anion. In collaboration with Hua Guo (New Mexico), the results were compared to full dimensional quantum dynamics calculations on *ab initio* potential energy surfaces (PESs). The comparison between theory and experiment for this system was impressive and was reported in Science. This included observation of stable and metastable complexes, the latter being Feshbach resonances supported by the open HF(ν) + OH product channels. The quantitative differences between theory and experiment indicate that the ground and excited state *ab initio* potential energy surfaces require further examination. Efficient infrared (IR) vibrational excitation of anions prior to injection into the EIBT was also demonstrated by recording an action spectrum of the autodetaching vibrational states of NO⁻. Data was then obtained examining the effect of excitation of the proton transfer vibration in (F-H-OH)⁻. Clear evidence for partitioning of vibrational energy to product translation was observed consistent with addition of the vibrational energy from the IR photon. Studies of the OH + CO reaction included experiments on the stability and dissociation dynamics of the formyloxyl radical that yielded product bending vibration resolved data for the carbon dioxide product. In collaboration with Al Wagner (Argonne) and others, the model previously introduced for tunneling dissociation of HOCO to H + carbon dioxide was tested using different *ab initio* PESs. The

model was found to provide a useful measure of the properties of the PES in the tunneling region. In a separate publication a detailed examination of the implications of the PPC experiments on the dynamics for dissociation into the OH + CO entrance channel was reported, showing that a more detailed theoretical examination of the cis – trans isomerization of HOCO and how that couples to the OH + CO entrance channel is needed.

Vibrational Dynamics and Dissociation of Ground-and Excited-State Clusters

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Funding: \$155,000 (2014)

PROGRAM SCOPE

Many excited-state processes involve the intersection of two electronic states along one or more coordinates, and the resulting interaction often creates a conical intersection between the two states. These structures are both intriguing and significant because the evolution of molecules through conical intersections determines the disposal of energy into dissociation fragments and the branching between different reaction pathways. This project studies the photodissociation of molecules that contain conical intersections to learn about the influence of vibrational excitation on their dissociation pathways. Our candidate molecules also form complexes with species such as CO, CO₂, C₂H₂, H₂O, and NH₃ that offer a range of bond strengths and geometries. The experiments use infrared excitation to prepare vibrationally excited molecules and complexes in combination with resonance enhanced multiphoton ionization and ion imaging detection to monitor the decomposition products. In the vibrationally mediated photodissociation experiments, a pulse of ultraviolet light, coming after the vibrational excitation pulse and before the detection pulse, transfers the vibrationally excited molecule to an electronically excited state where it dissociates. In many cases, it is possible to resolve quantum states of the detected product and infer the state of the unobserved product. Thus, the experiments discover the influence of vibrational excitation and complexation, individually and in combination, on the excited-state decomposition dynamics and pathways in a variety of molecules. It is even possible that the combination of electronic and vibrational excitation will initiate new reactions within the complexes. The experiments can identify dissociation pathways, discover the factors that control the course of decompositions, and test theoretical models of the dissociation of energized molecules.

FY 2014 HIGHLIGHTS

One of our primary accomplishments in 2014 was the study of the vibrational predissociation dynamics of the hydrogen-bonded 3-aminophenol-ammonia cluster (3-AP-NH₃) in the OH stretching and NH stretching regions. The vibrational energy is sufficient to dissociate the cluster into its constituent 3-AP and NH₃ monomers, and we detect the 3-AP fragments via (1+1) resonance-enhanced multiphoton ionization (REMPI). The distribution of vibrational-state population of the 3-AP fragment suggests the presence of two distinct dissociation pathways. The first dissociation channel produces a broad, unstructured predissociation feature in the REMPI-action spectrum after excitation of any of the O-H or N-H stretching vibrations, suggesting a nearly statistical dissociation pathway with strong coupling of the vibrations in the cluster during the predissociation. The second dissociation channel produces sharp

features on top of the broad predissociation features, but only following excitation of the OH stretch or the symmetric NH₃ stretch in the cluster. This striking mode-specificity is consistent with strong coupling of these two modes to the dissociation coordinate (the O-H...N bond). The measurements show that vibrational excitation is driving the isomerization of the trans-isomer to the cis-isomer in the course of the dissociation of the cluster.

Bimolecular Dynamics of Combustion Reactions

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

The aim of this research program is to better understand the mechanisms and product energy disposal in elementary bimolecular reactions fundamental to combustion chemistry. Using the crossed molecular beams method, the angular and velocity distributions of neutral products from single reactive collisions are measured using VUV laser ionization methods.

FY 2014 HIGHLIGHTS

During this funding period, we have further developed vacuum ultraviolet (VUV) generation by four-wave mixing of collimated (i.e., unfocussed) nanosecond laser pulses. Using our rotatable source crossed beams apparatus, we employ universal pulsed photoionization detection, typically using 0.1 mJ pulses at 9.9 eV (125 nm). We have recently studied the reactions of phenyl radicals with propene, trans 2-butene, and molecular oxygen. We have developed a technique for producing radiation extending into the extreme ultraviolet (XUV; $\lambda < 110$ nm) with higher conversion efficiencies than previously reported. Our method involves noncollinear phasematching of focused lasers in laser vaporized mercury (Hg) at room temperature. This approach easily facilitates windowless operation. Furthermore, using noncollinear phasematching, the short wavelength radiation is spatially isolated from the residual UV and visible beams without need for lossy optical elements such as windows, lenses, and gratings. Our approach using "soft" single photon pulsed ionization allows product molecules to drift to a triply differentially pumped detector before ionization, spreading out due to their velocities. This method is well suited for experiments using pulsed radical sources. In contrast to ion imaging or Rydberg tagging, where VUV is introduced into the high-pressure molecular beam crossing region, no interference from photodissociation or ion-molecule reactions is observed. As illustrated in our studies of phenyl radical reactions, the high ionization efficiency and low background leads to quite high signal to noise ratios. However, the need to scan the laser delay to measure product TOF distributions represents the key remaining limitation. To address this, we have initiated the development of a new detection method employing coaxial universal photoionization of products from crossed beam reactions within an ion guide. This method promises to dramatically improve detection sensitivity.

EARLY CAREER: Vibrational Spectroscopy of Transient Combustion Intermediates Trapped in Helium Nanodroplets

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Funding: \$150,000 (2014)

PROGRAM SCOPE

The objective of this research is to isolate and stabilize transient intermediates and products of prototype combustion reactions. This will be accomplished by Helium nanodroplet isolation (HENDI) spectroscopy, a novel technique where liquid helium nanodroplets freeze out high energy metastable configurations of a reacting system, permitting infrared spectroscopic characterizations of products and intermediates that result from hydrocarbon radical reactions with molecular oxygen and other small molecules relevant to combustion environments. The majority of these transient species have never been directly observed in traditional spectroscopy experiments. HENDI spectroscopy will be used to carry out the first direct observation of the elusive hydroperoxyalkyl radical (QOOH) and its oxygen adducts (O_2QOOH), important in the low-temperature hydrocarbon oxidation chemistry associated with homogeneous charge compression ignition (HCCI) engines. HENDI will also be used to probe the outcome of the self-reactions of resonantly stabilized free radicals, which are important in the earliest stages of soot formation. Thus, these studies may lead to an improved understanding of the detailed mechanisms of hydrocarbon combustion, resulting in more accurate predictive combustion models. Furthermore, mid-infrared spectral signatures of important combustion intermediates will be obtained to develop laser diagnostic tools for modern chemical kinetics studies.

FY 2014 HIGHLIGHTS

We spectroscopically probed the outcome of the reaction between the propargyl radical (C_3H_3) and O_2 within He droplets. A pick-up technique was employed where He droplets doped with a propargyl radical (generated by pyrolysis of 1-butyne-4-nitrite) were sequentially doped with an O_2 molecule. The reaction carried out at 0.4 K resulted exclusively in the formation of the acetylenic-trans-propargyl peroxy radical ($HC\equiv C-CH_2-OO\bullet$). This work helped to elucidate the shape of the entrance channel on the potential energy surface, as it was unclear whether or not there exists a small barrier to formation of the peroxy species. The rapid cooling afforded by the He droplets motivates the conclusion that if a barrier does indeed exist, it is too small to kinetically stabilize a van der Waals complex between C_3H_3 and O_2 . MRCI computations carried out in collaboration with Stephen Klippenstein and co-workers indicate that the reaction is barrierless, similar to alkyl + O_2 reactions. High resolution infrared spectra were obtained for the allyl radical (C_3H_5) and the products of the He-mediated reaction between allyl and O_2 . In the IR spectrum of He-solvated allyl, we observed rovibrational bands near the reported band origins in previous high resolution gas-phase studies. In addition to the fundamental CH stretching modes, four other bands were assigned to the allyl radical using a consistent set of rotational constants. Indeed, it was observed in the gas-phase studies that the CH stretch bands are heavily perturbed, but no explanation was given as to the nature of the perturbations. The lower temperature of the He droplets greatly decreases the number of populated rovibrational levels, and aided by anharmonic frequency computations and the resolved rotational substructure, we assigned the ν_1 (a_1), ν_3 (a_1), ν_{13} (b_2) fundamentals and the $\nu_{14}/(\nu_{15}+2\nu_{11})$ (b_2) and $\nu_2/(\nu_4+2\nu_{11})$ (a_1) Fermi dyads, in addition to an unassigned resonant resonant polyad near the ν_1 mode.

Spectroscopic and Dynamical Studies of Highly Energized Small Polyatomic Molecules

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Funding: \$160,000 (2014)

PROGRAM SCOPE

Tunable laser and Chirped Pulse millimeter-Wave spectroscopies are used to examine the structure and dynamics of highly energized, small polyatomic, combustion relevant molecules. Dynamical processes include unimolecular isomerization, photofragmentation, pyrolysis, predissociation, and Intramolecular Vibrational Redistribution. Particular emphasis is placed on mechanistic models of dynamics rather than merely numerical or statistical descriptions.

FY 2014 HIGHLIGHTS

The 2014 highlights of the DOE-supported research include:

1. Discovery and exploitation of the spectroscopic signature of the vibrational states proximal to an isomerization barrier. This signature is a dip in the vibrational level spacing. Examples include the S_1 electronic states of acetylene and HCN.
2. Calculation of full dimensional Franck-Condon factors for an electronic transition between bent and linear geometry electronic states. A new propensity rule is discovered for the Franck-Condon brightness of transitions, which simplifies the assignment of S_1 - S_0 transitions in acetylene.
3. Level-specific predissociation rates are discovered in the S_1 state of acetylene by comparing the intensity of fluorescence from intact HCCH to that of the H atom photofragment. This discovery was facilitated by the use of H atom 3d-2p H laser induced fluorescence.
4. IR-UV double resonance studies of the C-state of SO_2 provide detailed energy level structure that permits a vibronic coupling explanation for the apparent asymmetric equilibrium structure of the C-state.
5. Chirped Pulse millimeter-Wave spectroscopy has been used to document the mechanisms of pyrolysis reactions.

Spectroscopy and Kinetics of Combustion Gases at High Temperatures

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PROGRAM SCOPE

This program involves two complementary activities: (1) development and application of cw laser absorption methods for the measurement of concentration time-histories and fundamental spectroscopic parameters for species of interest in combustion chemistry; and (2) shock tube studies of reaction kinetics relevant to combustion mechanisms. These activities are focused on the study of small ketones and aldehydes (e.g. acetaldehyde, propanal, and 2-butanone) and their reactions. A deeper understanding of and strong constraints on the pyrolysis and oxidation kinetics of ketones and aldehydes is possible if the time-histories of individual species can be measured during chemical reactions. In addition to the diagnostics we currently have in this area, two other species are being investigated in the spectroscopic portion of the research: CO (whose sensitive detection is now possible because of the availability of QC lasers in the IR near 4600 nm) and CH₂O (which can be measured using ring-dye laser absorption in the UV near 305 nm or using DFG lasers in the IR near 3500 nm). Accurate modeling of oxygenate kinetics requires accurate knowledge of key radical reaction rates. However, the values of many key reaction rate constants used in current oxygenate mechanisms are based on theoretical estimates only and this can greatly degrade the confidence in these models. The kinetics portion of this program is focused on the measurement of reaction rates of selected oxygenate species with OH. This combination of spectroscopic and kinetics studies should provide a strong, and needed, database toward the development and refinement of oxygenate fuel models. It should also provide a better understanding of the combustion chemistry of individual ketone and aldehyde species, whose health and pollution roles in engine emissions are of increasing interest.

FY 2014 HIGHLIGHTS

A direct measurement for the rate constant of the acetone dissociation reaction, $\text{CH}_3\text{COCH}_3 = \text{CH}_3\text{CO} + \text{CH}_3$, was conducted behind reflected shock wave, utilizing a sub-ppm sensitivity CO diagnostic achieved by cavity-enhanced absorption spectroscopy (CEAS). By investigating the clean pyrolysis of less than 20ppm acetone in argon, the current experiment eliminated the influence from secondary reactions and temperature change. For the first time, the acetone dissociation rate constant was directly measured over 5.5 orders of magnitude with high degree of accuracy. This result was seen to agree with most previous studies, and has bridged the gap between their temperatures and pressures conditions. The current work also served as an example demonstration of the potential of using the CEAS technique in shock tube kinetics studies. The rate constant of the H-abstraction reaction of formaldehyde by hydrogen atoms (H), $\text{CH}_2\text{O} + \text{H} = \text{H}_2 + \text{HCO}$, has been studied behind reflected shock waves using a sensitive mid-IR laser absorption diagnostic for CO, over temperatures of 1304 - 2006 K and at pressures near 1 atm. C₂H₅I was used as an H-atom precursor and 1,3,5-trioxane as the CH₂O precursor, to generate a well-controlled CH₂O/H reacting system. By designing the experiments to maintain relatively constant H-atom concentrations, the current study significantly boosted the measurement sensitivity of the target reaction and suppressed the influences of interfering reactions. A transition-state-theory (TST) calculation, using the CCSD(T)-F12/VTZ-F12 level of theory, is in good agreement with the shock tube measurement and extended the temperature range of the current study to 200 - 3000 K.

Kinetics and Product Channel Studies in Combustion Chemistry

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Funding: \$233,000 (2014-2016)

PROGRAM SCOPE

This project involves the use of high resolution infrared laser spectroscopy to probe the products of chemical reactions and photochemistry relevant to the combustion chemistry of nitrogen-containing compounds. Emphasis is placed on obtaining reliable quantitative information on product yields, especially in reactions that have more than one possible product channel. When appropriate, we also perform *ab initio* calculations of the potential energy surfaces of some of these reactions.

FY 2014 HIGHLIGHTS

Work during fiscal year 2014 has concentrated on experimental work on the photochemistry of fulminic acid (HCNO). Fulminic acid is an intermediate in acetylene combustion, and is the less stable isomer of isocyanic acid (HNCO). Kinetics of HCNO reactions have been studied in our laboratory for the past decade, but only recently have we investigated the photolysis channels. Initial work used 248 nm photolysis wavelength, and more recent work has used 193 nm. We find a rich photochemistry with this molecule, with five measurable photochemical product channels. Although all channels are active at both photolysis wavelengths, there are significant differences in the product yields.

Probing the Reaction Dynamics of Hydrogen-Deficient Hydrocarbon Molecules and Radical Intermediates via Crossed Molecular Beams

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Funding: \$171,000 (2014)

PROGRAM SCOPE

The objectives of this project are to understand the formation mechanisms of bicyclic and tricyclic polycyclic aromatic hydrocarbons (PAHs) in combustion processes of hydrocarbon-based fuel. The formation and growth mechanisms of PAHs is an unsolved problem in the combustion chemistry community. To achieve these objectives, we will experimentally explore the energetics, chemical dynamics, potential energy surfaces (PESs), and reactions of key representatives of resonantly stabilized free radicals (RSFRs) and of aromatic radicals (ARs) with hydrocarbon molecules utilizing the crossed molecular beam approach. Our studies focus on four key systems: First, we untangle the collision energy dependent reaction dynamics of RSFRs [propargyl (H_2CCCH ; C_3H_3), cyclopentadienyl ($\text{c-C}_5\text{H}_5$), benzyl ($\text{C}_6\text{H}_5\text{CH}_2$; C_7H_7) and tolyl ($\text{C}_6\text{H}_5\text{CH}_3$; C_7H_7) with benzene (C_6H_6), vinylacetylene (C_4H_4), and acetylene (C_2H_2), respectively. These experiments access the C_9H_9 PES and investigate the formation of the bicyclic indene molecule (C_9H_8). Second, we aim to unravel the reaction dynamics of the key RSFR 1,2,3-butatrien-1-yl (H_2CCCCH ; $\text{i-C}_4\text{H}_3$) with benzene (C_6H_6) accessing the C_{10}H_9 PES. This study probes the formation of the bicyclic naphthalene molecule (C_{10}H_8). Third, we will expose the reaction dynamics of key ARs [1- and 2-naphthyl (C_{10}H_7)] with vinylacetylene (C_4H_4) accessing the $\text{C}_{14}\text{H}_{11}$ PES. These studies investigate the synthesis of the tricyclic anthracene/phenanthrene molecules ($\text{C}_{14}\text{H}_{10}$). Finally, we reveal the reaction dynamics of key ARs with hydrocarbon molecules, i.e. 1- and 2-naphthyl (C_{10}H_7) with methylacetylene/allene (C_3H_4) and of 2- and 7-indenyl (C_9H_7) with vinylacetylene (C_4H_4) accessing various

parts of the C₁₃H₁₁ PES. These studies investigate the formation of the tricyclic fluorene/¹H-benz[f]indene/¹H-benz[e]indene, as well as of 1H-phenalene (C₁₃H₁₀). The results of the scattering experiments are combined with *ab initio* calculations (Alexander Mebel) and with flame modeling.

FY 2014 HIGHLIGHTS

The objectives of this project were to understand the formation mechanisms of bi- and tricyclic polycyclic aromatic hydrocarbons (PAHs) in combustion processes of hydrocarbon-based fuel utilizing cross beam method: First, resonantly stabilized free radicals (RSFRs) C₅H₅ isomers 1- and 3-vinylpropargyl, C₆H₅ isomers other than phenyl and non-cyclic C₇H₇ isomers were observed in the reactions of dicarbon (C₂) with propene C₃H₆, C₄H₆ isomers (1-butyne, 2-butyne and 1,2-butadiene), and 1,3-pentadiene, respectively. Second, monocyclic aromatic and their radicals (ARs), the benzyl radical (C₇H₇) and toluene (C₇H₈) were formed by reactions of dicarbon C₂ and methylidene (C₂H) with isoprene (C₅H₈), respectively. Third, reactions of the phenyl radical with 1,2-butadiene (C₄H₆), 1,3-pentadiene and isoprene (C₅H₈) and phenylacetylene (C₈H₆) formed 2-phenyl-1,3-butadiene, PAHs 2- and 1-methyl-1,4-dihydronaphthalene and a range of substituted biphenyls. Fourth, reactions of para-tolyl with allene and methylacetylene (C₃H₄), vinylacetylene (C₄H₄), 1,3-butadiene (C₄H₆), 1,2-butadiene (C₄H₆) and isoprene, formed 5- and 6-methylindene (C₁₀H₁₀), 2-methylnaphthalene (C₁₁H₁₀), 6-methyl-1,4-dihydronaphthalene (C₁₁H₁₂), tolyl-1,3-butadiene (C₁₁H₁₂) and dimethyldihydronaphthalenes (C₁₂H₁₃), respectively. Finally, several investigations were conducted using a pyrolysis nozzle at the Advance Light Source, Berkeley. The phenyl radical reaction with 1,3-butadiene formed a range of C₉H₈ isomers with indene being insignificant. The phenyl reaction with two acetylene molecules formed first phenylacetylene (C₈H₆) then naphthalene (C₁₀H₈) revealing the HACA mechanism. Finally the reaction of phenyl with oxygen at two temperatures was investigated yielding 18 products along with their temperature dependent branching ratios.

Intermolecular Interactions of Hydroxyl Radicals on Reactive Potential Energy Surfaces

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PROGRAM SCOPE

The DOE-BES research program in the Lester laboratory aims to characterize important, yet often elusive, reaction intermediates in combustion chemistry using novel spectroscopic and dynamical methods. A robust, state-selective ionization scheme is being developed for the hydroxyl radical, a key oxidant in combustion, by combining OH A-X excitation with VUV ionization. The research is aimed at understanding the ionization step via autoionizing Rydberg states and utilizing the novel OH detection scheme in various applications. Carbonyl oxides of general form R₁R₂COO, important intermediates in tropospheric hydrocarbon oxidation and some combustion reactions, are also being investigated through their UV spectroscopy and photochemistry. The research is focused on the UV photodissociation dynamics of prototypical carbonyl oxides to O¹D and O³P products in order to determine dissociation energies and dynamical pathways involving multiple potential energy surfaces.

FY 2014 HIGHLIGHTS

This laboratory utilized a new velocity map imaging apparatus to study the UV photodissociation dynamics of the simplest Criegee intermediate CH₂OO. Here, the velocity and angular distributions of O¹D photofragments are characterized following UV excitation of CH₂OO on the B¹A' ← X¹A' transition. An anisotropic angular distribution indicative of prompt dissociation yields the orientation of the transition dipole moment, which reflects the π* ← π character of the electronic transition associated with the COO group. The total kinetic energy release distributions obtained at several photolysis wavelengths provide detail on the internal energy distribution of the formaldehyde cofragments and the dissociation energy of CH₂OO X¹A' to O¹D + H₂CO X¹A₁. A common termination of the total kinetic energy distributions, after accounting for the different excitation energies, gives an upper limit for the CH₂OO X¹A' dissociation energy of D₀ < 54 kcal mol⁻¹, which compares favorably with theoretical predictions including high level multi-reference *ab initio* calculations. A complementary theoretical study utilized wave packet dynamics on the excited B-state to examine the dissociation dynamics of CH₂OO. These calculations indicate that dissociation occurs promptly and primarily along the diabatic B-state potential to O³P + H₂CO a³A' products. A much smaller yield is predicted for the lowest spin-allowed channel to O¹D + H₂CO X¹A' products, which arises from couplings between multiple diabatic states.

Computational Flame Diagnostics for Direct Numerical Simulations with Detailed Chemistry of Transportation Fuels

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

The goal of the proposed research is to create computational flame diagnostics that are rigorous numerical algorithms to detect critical flame features, such as ignition, extinction, and premixed and non-premixed flamelets, and to understand the underlying physicochemical processes controlling limit flame phenomena, flame stabilization, turbulence-chemistry interactions and pollutant emissions etc. The goal will be accomplished through an integrated effort on mechanism reduction, direct numerical simulations (DNS) of flames at engine conditions, computational diagnostics, and DNS data mining. The computational diagnostics are primarily based on the chemical explosive mode analysis (CEMA) and a recently developed bifurcation analysis using datasets from first-principle simulations of 0-D reactors, laminar flames, and 2-D and 3-D direct numerical simulations (DNS) (collaboration with Dr. J.H. Chen at Sandia). Non-stiff reduced mechanisms for transportation fuels amenable for 3-D DNS are developed through graph-based methods and timescale analyses. DNS for premixed and non-premixed flames at diesel jet and homogeneous charge compression ignition (HCCI) engine conditions using the non-stiff reduced chemistry are performed through a collaborative effort (with J.H. Chen and C.S. Yoo). The flame structures, stabilization mechanisms, local ignition and extinction etc., and the rate controlling chemical processes are unambiguously identified.

FY 2014 HIGHLIGHTS

Reduced mechanisms for a variety of practical engine fuels are developed based on directed relation graph (DRG), analytically solved linearized quasi steady state approximations, and dynamic chemical stiffness removal etc., for dimethyl ether (DME), ethanol-air with NO_x formation, primary reference fuels (PRF), and a ternary biodiesel surrogate. The reduced mechanisms are employed in Sandia's (J.H. Chen) DNS of lifted flames, HCCI and SACI simulations. A reduced mechanism for n-dodecane as diesel surrogate was developed through collaboration with S. Som at Argonne for diesel engine simulations by the engine combustion network (ECN). A dynamic adaptive chemistry (DAC) method is developed to expedite time integration of chemically reacting systems based on DRG. The DAC method is applied in the Strang splitting schemes, and a second order accuracy in time-integration was achieved in simulations of 1-D premixed flames of methane-air. A speedup factor of about 30 is achieved using DAC for HCCI combustion of isooctane-air in a partially stirred reactor, and even larger speedup factors are achieved after combining DAC with in-situ adaptive tabulation (ISAT). A method of bifurcation analysis (BA) is developed based on the description of extinction and ignition states as bifurcation points on the S-curves of steady state combustion. Reactions important to ignition and extinction are systematically identified based on their contributions to the bifurcation states. BA is shown to be overall as effective as the brute-force global sensitivity analysis while featuring significantly higher computational efficiency. Furthermore, DNS data for the ethanol, DME, PRF and biodiesel flames are systematically diagnosed with chemical explosive mode analysis (CEMA) to extract critical flame features, such as premixed flame fronts, local ignition and extinction. Different modes for premixed flame propagation (auto-igniting fronts vs. deflagration waves) are further identified.

Advanced Nonlinear Optical Methods for Quantitative Measurements in Flames

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PROGRAM SCOPE

Nonlinear optical techniques such as laser-induced polarization spectroscopy (PS), resonant wave mixing (RWM), and electronic-resonance-enhanced (ERE) coherent anti-Stokes Raman scattering (CARS) are techniques that show great promise for sensitive measurements of transient gas-phase species, and diagnostic applications of these techniques are being pursued actively at laboratories throughout the world. The objective of this research program is to develop and test strategies for quantitative concentration and temperature measurements using nonlinear optical techniques in flames and plasmas. We have continued our fundamental theoretical and experimental investigations of these techniques. We have also initiated both theoretical and experimental efforts to investigate the potential of femtosecond (fs) laser systems for sensitive and accurate measurements in gas-phase media. Our initial efforts have been focused on fs CARS, although the systems will be useful for a wide range of future diagnostic techniques involving two-photon transitions.

FY 2014 HIGHLIGHTS

In the last year we have demonstrated the acquisition of single-shot temperature measurements at data rates of 5 kHz in highly turbulent, swirl-stabilized methane-air flames. The fs CARS measurements exhibited high signal-to-noise ratios and temperatures were extracted from nearly every laser shot. Over the past year we have continued our two-color PS measurements. We developed and optimized a new laser system for the two-color PS measurements of nitric oxide featuring two injection-seeded optical parametric generator/pulsed dye amplifier (OPG/PDA) systems, both operating near 452 nm. Collision-induced resonances were clearly observed with this system. We are investigating the physics of both fs CARS and two-color PS by direct numerical integration (DNI) of the time-dependent density matrix equations for the resonant interaction. Significantly fewer restrictive assumptions are required using this DNI approach compared with the assumptions required to obtain analytical solutions. We are concentrating on the accurate simulation of two-photon processes, including Raman transitions, where numerous intermediate electronic levels contribute to the two-photon transition strength. We have made significant progress in the last year on modeling two-color PS of atomic hydrogen, and are obtaining good agreement between experiment and modeling. We have also developed a new technique for simultaneous pure rotational and vibrational CARS, and we have continued to develop and apply this new technique during the past year. This method takes advantage of a two-beam phase-matching scheme for pure rotational CARS.

Detection and Characterization of Free Radicals Relevant to Combustion Processes

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

Combustion processes have been studied for many years, but the chemistry is very complex and yet to be fully understood. Modern computer codes for its modeling typically employ hundreds of reaction steps with a comparable number of chemical intermediates. The predictions of such models are obviously limited by the dynamical and mechanistic data that are input. Spectroscopic identifications and diagnostics for the chemical intermediates in the reaction mechanisms constitute an important experimental benchmark for the models, as well as providing molecular parameters that are “gold standards” against which quantum chemistry computations of molecular properties may be judged. Our recent work has emphasized the spectroscopy of reactive organic radicals, like peroxides and related molecules, which are known to be key intermediates in combustion reactions as well as being present in atmospheric oxidation of fuels and other organic compounds. We develop the basic spectral information required to produce highly sensitive and selective diagnostics for these reactive intermediates. Moreover the spectroscopic data directly characterizes these species which can be critical for benchmarking *ab initio* computer codes that calculate these quantities, as well as other properties not easily subject to experimental verification.

FY 2014 HIGHLIGHTS

It is well known that larger chain alkanes ($> C_5$ - C_{10}) are important components of gasoline and diesel fuels. Our previous CRDS spectroscopy of combustion intermediates has been limited to the $\tilde{A}-\tilde{X}$ transition of peroxy radicals with ≤ 5 carbon atoms. Recently we have extended our observations to larger chain intermediates, i.e. hexyl, heptyl, octyl, nonyl, and decyl peroxy radicals produced from the C_6 - C_{10} alkanes. In these experiments the peroxy radicals are formed from H atom extraction by Cl atom attack (simulating OH attack in combustion) on the corresponding hydrocarbon followed by reaction with O_2 . It is possible to form multiple isomers of peroxy radicals as there are several unique hydrogen atoms that can be abstracted by the Cl atom. Structural/spectral relationships that have been derived from our earlier data on C_1 - C_5 hydrocarbons, allow assignments of the C_6 - C_{10} peroxy radical spectra which are mostly too large for accurate predictions from electronic structure calculations. Particularly interesting are the spectra of the peroxy radicals resulting from the oxidation of two isomers of octane, n-octane and iso-octane, the latter the standard (100) for the rating of commercial gasolines. We observed that n-octane, like the other larger alkanes studied, produces almost exclusively the sec isomers of the corresponding peroxy radical. On the other hand, in the case of iso-octane only the pri and tert isomers of the corresponding peroxy radicals are observed.

Dynamics of Activated Molecules

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

This research program investigates the dynamics of reactive and non-reactive processes of highly excited gas-phase molecules that are involved in combustion chemistry. Elevated temperatures in combustion environments produce vibrationally excited molecules (with $E > 100$ kcal/mol) that have enhanced reaction rates. The means by which molecular energy is available for chemistry is governed by the quantum-mechanical nature of molecular vibrations. Collisional deactivation of highly excited species competes directly with reactive channels and can lower reaction rates if sufficient energy is removed through collisions. In our experiments, highly vibrationally excited molecules are prepared by pulsed UV excitation, followed by rapid radiationless decay. High-resolution transient IR absorption spectroscopy is used to characterize the kinetics of quantum-state resolved energy flow that occurs when highly excited molecules undergo inelastic or reactive collisions. Doppler-broadened IR line profiles of nascent collision products provide a direct measure of how the exchanged energy is partitioned into vibrational, rotational and translational degrees of freedom. The molecular systems under investigation are chosen to reveal how the molecular structure and charge distribution of the high energy molecules and the energy-accepting molecules impact the energy transfer dynamics. These studies yield information about the energy transfer mechanism and the intermolecular potential energy surface that controls the dynamics.

FY 2014 HIGHLIGHTS

The presence of near-resonant vibrational pre-dissociation in collisions of pyrazine(E) with HCl was investigated as the source of an unusual isotope effect in pyrazine/ HCl and DCl collisions. We removed the near-resonant mode by switching to pyrazine-d₄ as an energy donor. The frequency of HCl (2949/cm) is close to pyrazine-h₄ stretch modes (3040-3069/cm) but far from pyrazine-d₄ C-D stretches (2270-2290/cm). We found that J-dependent recoil energies for pyrazine-d₄/HCl collisions are similar to those for pyrazine-h₄, indicating that near-resonant effects are not responsible for the dynamics. Additional evidence that vibrational pre-dissociation is not active comes from similarities in the HCl (v=1) product state distributions for both donors. We conclude that differences in zero-point energies for HCl and DCl collision complexes limit the HCl motion in collisions and reduces the opportunity for multiple encounters during the collisional quenching. A second project explored how methane collisionally quenches pyrazine(E). Methane is the simplest hydrocarbon and is important in combustion. Despite being the simplest hydrocarbon, methane has a complex IR spectrum and our initial task was to sort out the effects of vibration-rotation coupling, centrifugal distortion and nuclear spin statistics on the IR spectrum. Transient measurements showed that methane is scattered in three vibrational states: (0000), (0100) and (0010). No scattering was seen into the higher energy (0001) state. Rotational and translational energy measurements (600 K and 530-780 K for J=2-15, respectively) show that scattering of methane (0000) occurs by impulsive collisions and is the primary pathway quenching pathway (85% of collisions). The (0100) and (0010) product states have cooler rotational (320 K) and translational (380 K) distributions, indicating a long range mechanism. Rate measurements indicate that the (0100) and (0010) states account for 15% of collisions.

Spectroscopy, Kinetics, and Dynamics of Combustion Radicals

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PROGRAM SCOPE

This report covers the results from the second year of a three-year program for elucidation of spectroscopy, kinetics and structural dynamics of combustion radicals. Both the dynamics and spectroscopy of jet cooled hydrocarbon transients have been explored, utilizing i) high resolution IR lasers, ii) slit discharge sources for formation of jet cooled radicals, and iii) high sensitivity detection with direct laser absorption methods near the quantum shot noise limit. The advantage of this experimental combination is that such highly reactive radical transients can be made under high pressures/temperatures characteristic of combustion conditions, with the resulting species rapidly cooled to T = 10-15K in the slit supersonic expansion for maximal spectroscopic simplification. Four highlights from work over the last year are summarized below.

FY 2014 HIGHLIGHTS

Hydroxymethyl radical, CH₂OH, plays a critically role as a reactive intermediate in combustion. In addition to fundamental combustion processes, hydroxymethyl radical is an important intermediate for oxidative reactions occurring in the troposphere. For example, atmospheric scrubbing reactions of alkanes, alkenes, and alcohols all involve hydroxymethyl radical as a reactive intermediate.

Hydroxymethyl ($\bullet\text{CH}_2\text{OH}$), is predicted to have a slightly non-planar equilibrium structure with a low barrier across a Cs transition state due to OH internal rotation. This work has profited by the excellent vibrationally tagged double resonance ion depletion (DRID) studies of Reisler and coworkers on $\bullet\text{CH}_2\text{OH}$, which yielded structured rovibrational band contours in the CH and OH stretch regions limited by a 0.4 cm^{-1} laser linewidth. The present studies under sub-Doppler conditions promise to provide over 2 orders of magnitude improvement, which permit complete resolution and analysis of the underlying spectral structure due to end-over-end tumbling, internal OH rotor dynamics as well as coupling with CH/OH vibration modes. We have already made substantial progress, with initial spectral searches for CH_2OH in the symmetric CH_2 stretch region in a methanol doped He/Ne discharge. At sub-Doppler resolution, CH_2OH reveals a surprisingly intense spectrum, with typical S/N of 20:1, and $K_a = 0$ from 0 A-type rotational assignments, which provide first precision molecular constants for this oxyradical species. The transitions are fit to a Watson A-reduced symmetric top Hamiltonian to yield first precision experimental values for the ground state rotational constants as well as improved values for the symmetric stretch rotational constants and vibrational band origin. The results both complement and substantially augment previous spectral efforts as well as offer high resolution predictions for astronomical detection of CH_2OH radical in the mm-wave region.

Determination of Accurate Energetic and Spectroscopic Database for Combustion Radicals and Molecules by High Resolution Photoion-Photoelectron Methods

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PROGRAM SCOPE

The main goal of this research program is to obtain accurate thermochemical data, such as ionization energies, 0 K dissociative photoionization thresholds, 0 K bond dissociation energies, and 0 K heats of formation for molecular species and their ions of relevance to combustion chemistry. Accurate thermochemical and spectroscopic data for polyatomic molecules, including radical and cationic species, determined in the present study by high-resolution photoionization, photoelectron, and photodissociation methods are also used for benchmarking predictions of state-of-the-art *ab initio* quantum calculations. This effort is aimed to assist the development of the next generation of quantum computation procedures for providing more accurate energetic and structural predictions of neutral and ionic species.

FY 2014 HIGHLIGHTS

We have completed the high-resolution PFI-PE studies of a series of radicals, including propargyl radical (C_3H_3), allyl radical (C_3H_5), and halogen-substituted methyl radicals (CH_2Cl and CH_2Br).

Photoinitiated Reactions of Radicals and Diradicals in Molecular Beams

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PROGRAM SCOPE

Open shell species such as radicals and diradicals are central to reactive processes in combustion and environmental chemistry. Our program is concerned with photoinitiated reactions of hydroxyalkyl radicals and carbenes. The goal is to investigate the detailed dynamics of dissociation of free radicals and diradicals in which multiple pathways participate, including molecular rearrangements, and compare them with high-level calculations. Studies include unimolecular reactions on the ground state as well as photodissociation dynamics on excited Rydberg and valence states that involve multiple potential energy surfaces. Reactions are carried out in molecular beams using pulsed laser excitation, and products' quantum states are detected by time-sliced velocity map imaging.

FY 2014 HIGHLIGHTS

Recent experiments on the photodissociation of the hydroxymethyl radical have focused on excited states of the hydroxymethylene product, an elusive intermediate implicated in the unimolecular decomposition of formaldehyde and relevant to combustion processes. By monitoring the velocity and kinetic energy release of H photofragments generated by C-H bond breaking in the radical, we gain information on HCOH(D) products. For example, we have been able to provide new information on the trans- and cis-isomers of HCOH(D) with internal energies ranging from low rovibrational excitations to above their dissociation thresholds to H(D) + H(D)CO. The distinction between the cis and trans isomers becomes clearer when using different H/D isotopologs, which have different vibrational frequencies. The preference for generating the higher-lying cis-HCOH in the photodissociation has been predicted by calculations of the relevant conical intersections that lead to these isomers. We have also determined experimentally for the first time the singlet-triplet gap in HCOH and the energy difference between the triplet states of formaldehyde and hydroxymethylene. This information is derived from time-sliced velocity map imaging experiments, using a new design developed in our lab, which optimizes the velocity resolution in detecting H photofragments. One of the advantages of using the hydroxymethyl radical as a source of hydroxymethylene is that it has continuous absorption over a broad wavelength range, and thus the internal energy of HCOH can be increased progressively by accessing several Rydberg states of the precursor. Current experiments are aimed at developing more efficient sources of hydroxymethylene and its derivatives by using pulsed pyrolysis and photolysis of keto-carboxylic acids such as glyoxylic and pyruvic acids.

Universal and State-Resolved Imaging Studies of Chemical Dynamics

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PROGRAM SCOPE

This program is directed to building a fundamental understanding of chemical reaction dynamics with particular emphasis on elementary reactions and mechanisms important in predicting combustion chemistry. This research is conducted using state-of-the-art molecular beam machines and vacuum ultraviolet lasers in conjunction with DC slice ion imaging and other advanced spectroscopic techniques to study frontier areas in photodissociation, unimolecular decomposition, and bimolecular reactions. This program exploits recent advances in high-resolution slice ion imaging, in imaging applications of crossed molecular beam scattering, and in development of new experimental approaches, to extend the range of chemical dynamics studies into frontier areas. A key aspect of this effort is on combining universal probes providing a global perspective with high-resolution state-resolved probes yielding quantum mechanical detail, to develop a molecular-level understanding of chemical phenomena. Two important new experimental avenues are incorporated in the proposed studies. These include the development and application of strong-field ionization as a universal but selective probe of polyatomic reaction products and combustion intermediates, and chirped-pulse mm Wave spectroscopy in pulsed uniform supersonic flows, a powerful new approach that promises both structural and product branching information for unstable reaction intermediates and reaction products. These two novel approaches promise to open new windows into the details of the complex chemistry of combustion systems. The specific objectives of our program remain: to extend the range of powerful dynamics studies to more complex polyatomic systems; to identify novel reaction pathways such as roaming dynamics and characterize them in full detail; to identify transient species in combustion-related reactions; and to benchmark a range of theoretical methods. Our work often involves synergistic collaboration with leading theoreticians.

FY 2014 HIGHLIGHTS

Addition-elimination reactions are textbook reactions familiar to all chemists, where the final products are produced after the formation of a long-lived adduct. These reactions often compete with direct pathways to form the same products, as seen in the gas-phase for reactions of chlorine atoms with unsaturated hydrocarbons. Here, the precise pathway leading to release HCl from the initially-formed adduct was still a mystery. In imaging experiments, the A.G. Suits group studied the scattering distributions when beams of Cl atoms collide with butene molecules, and found both direct and indirect pathways with different energy dependence. They then turned to high-level theoretical calculations from A. M. Mebel to understand the reaction mechanisms. A careful theoretical analysis of the properties of the system revealed that, to decompose, the highly frustrated π adducts must undergo near-dissociation back to the starting reactants before eliminating HCl at the adjacent saturated sites. This is a clear example of roaming radical dynamics, now widely recognized in unimolecular reactions, showing that they play a central role in a broad class of bimolecular reactions as well.

A Novel Multiscale Simulation Strategy for Turbulent Reacting Flows

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PROGRAM SCOPE

Turbulent reacting flow remains a grand challenge problem from a modeling and simulation standpoint. Reynolds-Averaged Navier Stokes (RANS) techniques resort to modeling all timescales of the flow, and is not predictive for reacting flows. Large Eddy Simulation (LES) is a technique that resolves the large length/time scales of the flow while modeling unresolved scales, and has gained widespread adoption in the past 20 years. Direct Numerical Simulation (DNS) fully resolves all continuum length and time scales in the flow, but is restricted to simple flows at low Reynolds number due to its tremendous cost. The One-Dimensional Turbulence model provides an alternative to traditional CFD approaches that models the effect of turbulent eddies on the flow field, but in a single spatial dimension. ODT has been shown to capture salient features of a wide range of flow fields, and naturally captures the $-5/3$ energy cascade in isotropic turbulent flows. Additionally, ODT has been shown to capture challenging turbulence-chemistry interactions that govern extinction/reignition. Furthermore, ODT is significantly less expensive than other CFD approaches such as LES and DNS. However, due to its one-dimensional nature, ODT cannot capture multidimensional effects such as recirculation or some mechanisms of flame stabilization such as triple-flames. This project draws on the strength of the ODT model while seeking to overcome its weaknesses by forming a lattice of ODT domains which are fully coupled in their evolution. This provides a simulation approach that resolves the large scales of the flow (integral length and time scales) directly on the lattice while representing the small scales of the flow through each of the ODT lines. We will demonstrate the efficacy of the lattice-ODT approach on canonical flows such as isotropic turbulent decay prior to addressing more complicated turbulent reacting flow problems including lifted partially premixed flames.

FY 2014 HIGHLIGHTS

During FY 2014, we focused on developing the software to implement the modeling framework and scale it to several thousand processors. We employ a hybrid task and data parallelism approach which provides the opportunity for overlapping communication and computation. We considered strong and weak scalability at various lattice spacings, and demonstrated good strong and weak scalability. Because of the unique lattice structure of the approach, data structures and the associated communication patterns specific for this approach had to be developed. In addition to the focus on software design and scalability, we investigated the ability of the new formulation to simulate isotropic turbulence decay. This required significant effort to generate the initial conditions that were appropriate for the lattice, and consumed much more time than we anticipated. However, we are presently running preliminary studies on this. Finally, we have been implementing the required thermochemistry models to allow simulation of reacting flows with detailed kinetic mechanisms, thermodynamics and transport. This is nearly complete as well.

Developing a Predictive Model for the Chemical Composition of Soot Nanoparticles

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

Carbonaceous nanoparticles (CNPs) are formed in combustion environments and have significant impacts on society. A significant emission from internal combustion engines, CNPs pose a significant health hazard; CNPs are primarily composed of carcinogenic polycyclic aromatic hydrocarbons (PAHs) and have small size ($\leq 100\text{nm}$) that can increase particle toxicity. In flames, a substantial amount of effort has elucidated the gas-phase chemistry of CNP precursors such as acetylene and benzene, as well as the eventual growth of CNPs into larger soot particles. However, there is still substantial uncertainty concerning particle inception, or the transition from the gas-phase to solid-phase, which is a complex process involving both chemical and physical phenomena. Particle inception or nucleation has a significant impact on the growth of combustion-emitted particles, especially their size distribution and morphology. Moreover, the physiochemical properties of nanoparticles, including size and morphology, greatly influence their toxicology. The aim of this project is to investigate particle inception through the development and application of a novel and detailed theoretical model for CNP growth. The model will be guided and validated with experimental data produced at Sandia National Laboratories and Lawrence Berkeley National Lab. This work will provide novel insight into the size distributions and morphology of chemically grown CNPs in flames, both of which substantially impact physical agglomeration phenomena. The current approach is novel, as it implements a highly flexible algorithm for chemical reactions in significantly greater detail than current models. Moreover, the model considers arbitrary CNP structure rather than, for example, focusing on planar CNP structures. Most importantly, this computational code has been developed to be highly extensible, in order to incorporate physical coalescence of CNPs, as well as to support the implementation of any arbitrary chemistry.

FY 2014 HIGHLIGHTS

We have combined theoretical approaches and experiments to gain new insight into the mechanisms of PAH growth and soot formation. The experimental approach has involved aerosol-mass spectrometry in conjunction with vacuum-ultraviolet photoionization of volatile species vaporizing from particles sampled from simple hydrocarbons, such as C_2H_2 counter-flow diffusion flame at nearly atmospheric pressure (700 Torr). The mass spectra contained a large distribution of peaks, highlighting the importance of small building blocks and showing a variety of chemical species that extended beyond the traditional classification of PAHs based on thermodynamic stability. We developed a new code to describe the chemical growth of PAHs based on stochastic simulations. The code was named SNAPS as it stands for stochastic nanoparticle simulator. The code has been used to interpret the experimental data in order to provide better insight into the chemical composition of species associated with peaks in the measured mass spectra.

Publications resulting from this work are reported below:

1. S.A. Skeen, H.A. Michelsen, Kevin R. Wilson, Denisia M. Popolan, A. Violi, N. Hansen, "Near-Threshold Photoionization Mass Spectra of Combustion-Generated High-Molecular-Weight Soot Precursors", *J. Aerosol Science* 58: 86-102 (2013).
2. J.Y. Lai, P. Elvati, A. Violi, "Stochastic Atomistic Simulation of Polycyclic Aromatic Hydrocarbon Growth in Combustion", *Phys. Chem. Chem. Phys.*, 16 (17), 7969 – 7979 (2014).
3. K.O. Johansson, J. Lai, S.A. Skeen, K.R. Wilson, N. Hansen, A. Violi and H.A. Michelsen "Soot precursor formation and the breakdown of the stabilomer concept", *Proceedings of the Combustion Institute* 35 (2): 1819-1826 (2015).

4. J.S. Lowe, J.Y.W. Lai, P. Elvati and A. Violi. "Towards a predictive model for polycyclic aromatic hydrocarbon dimerization propensity" Proceedings of the Combustion Institute: 35(2): 1827-1832 (2015).

The Effects of Oxygenated Fuel Compound Structure on Combustion and Pollutant Reaction Chemistry

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Funding: \$145,000 (2014)

PROGRAM SCOPE

Recent research into combustion chemistry has shown that reactions at "low temperatures" (700 – 1100 K) have a dramatic influence on ignition and combustion of fuels in virtually every practical combustion system. A powerful class of laboratory-scale experimental facility that can focus on fuel chemistry in this temperature regime is the rapid compression facility (RCF), which has shown a remarkable ability to examine the details of fuel chemistry in this important regime. Our past studies have advanced our understanding of low temperature chemistry of important fuel compounds and has identified areas of high uncertainty for further research. In particular, we have shown how factors including fuel molecular structure, the presence of unsaturated C=C bonds, and the presence of alkyl ester groups influence fuel auto-ignition and produce variable amounts of negative temperature coefficient behavior of fuel ignition. We have also reported new discoveries of synergistic ignition interactions between alkane and alcohol fuels, with both experimental and kinetic modeling studies of these complex interactions. This project focuses on further clarifying the effects of molecular structure including carbon bond saturation, through low temperature combustion chemistry studies of esters, alkanes, alkenes, and alcohols. Studies of synergistic fuel component interactions are also of interest in this project. Gas-speciation analysis is applied to directly identify decomposition and oxidation pathways and to measure sentinel species for particulate production (e.g. propene).

FY 2014 HIGHLIGHTS

Despite the interest in production and combustion of other alcohols, the dominant alcohol fuel utilized in the U.S. remains ethanol. There have been numerous studies of ethanol combustion behavior and kinetics, and during the past year the University of Michigan rapid compression facility (UM RCF) was used to explore new conditions at higher pressures (~3-10.5 atm) and lower temperatures (less than 1200 K) than previous studies. The results quantify the effects of pressure and temperatures at conditions relevant to modern engines. The effects of bond structure on combustion chemistry remains a topic of considerable interest to quantify fuel reactivity and validate and develop reaction theory. Last year we completed ignition and speciation studies of the three trans hexene isomers: 1-hexene, trans-2-hexene and trans-3-hexene. Ignition delay time data were acquired using the UM RCF over a range of state and mixture conditions for each of these reference compounds. Mass sampling and gas chromatography were applied to quantify the stable intermediates present during ignition. The results of our hexene isomers study clearly show the significant changes (greater than a factor of 2 for some species concentrations) in reaction pathways that occur due to the differences in the location of the carbon-carbon double-bond in these C₆H₁₂ compounds. Despite excellent agreement with predictions of

reactivity, existing reaction mechanisms do not appear to accurately capture the quantitative differences in reaction pathways. These studies emphasize the need for accurate reaction mechanisms for these fundamental building blocks of real fuels. Another highlight of 2014 was a study to revisit n-butanol ignition chemistry led by Dr. Darshan Karwat (a graduate of UM, now with the DOE) in partnership with Drs. Stephen Klippenstein and Michael Davis of Argonne National Laboratory. The outcomes highlight the utility of theoretical chemical kinetics studies for combustion modeling.

Isomer-specific Spectroscopy and Pyrolysis of Model Aromatic Fuels

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Funding: \$574,773 (2014-2017)

PROGRAM SCOPE

The chemical complexity of hydrocarbon fuels and the fast-expanding list of potential plant-derived biofuels offer a challenge to the scientific community seeking to provide a molecular-scale understanding of their combustion. The development of accurate combustion models stands on a foundation of experimental data on the kinetics and product branching ratios of individual reaction steps. Spectroscopic tools need to continue to be developed to selectively detect and characterize the widening array of fuel components and the reactive intermediates they generate upon pyrolysis and combustion. There is growing recognition that a key component of future progress in the field is the development of detection schemes that are isomer-specific and even conformation-specific. This project uses an array of laser-based and broadband microwave methods to carry out conformation-specific and isomer-specific spectroscopy on key fuel components and the reactive intermediates formed during their pyrolysis and combustion.

FY 2014 HIGHLIGHTS

During FY 2014 we recorded alkyl CH stretch infrared spectra of a series of hydrogenated naphthalenes and naphthyl radicals formed and cooled in a supersonic expansion. Collaborating with Ned Sibert's group, we are developing a theoretical model that accounts quantitatively for the stretch-bend Fermi resonance in this traditionally challenging region of the spectrum to understand. We completed studies of the unusual spectroscopy of sinapoyl malate and its derivatives, which serves as a "sunscreen" for plants, and of model lignin dimers, both as neutrals and in complexes with alkali metal cations. These spectra show that sinapoyl malate is uniquely suited to its task, possessing an inherently broad UV spectrum that results in complete coverage of the UV-B region even under jet-cooled conditions in the gas phase. We have also used the combination of a hyperthermal nozzle and a broadband chirped-pulse Fourier transform microwave spectrometer to characterize the rotational spectroscopy and molecular structure of cyclopentadienone, a model anti-aromatic molecule that is a pyrolysis intermediate common to many biofuels. Finally, we have characterized state-specific vibronic coupling effects in asymmetric bichromophores that shed light on the electronic energy transfer between close-lying excited states.

DOE National Laboratories

Chemical Dynamics Beamline Facility

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Funding: \$1,164,000 (2014)

PROGRAM SCOPE

The primary purpose of this program is to support studies in chemical physics at the ALS by providing state-of-the-art experimental resources for visiting scientists and staff to undertake studies of fundamental chemical processes:

- To determine the microscopic details of the mechanisms and dynamics of primary dissociation processes and elementary chemical reactions.
- To explore the properties and decay dynamics of molecules in highly excited, transient, or metastable states.
- To study the structure, energetics and chemical reactivity of highly reactive polyatomic radicals, unusual transient species, droplets, aerosols, large biomolecules and clusters.
- To develop new spectroscopic and dynamical tools with charged particle imaging, molecular beams, and 2 color laser synchrotron pump-probe techniques.
- To pioneer new directions and developments in photoionization and photoelectron spectroscopy for the enriched understanding of fundamental properties of ions and molecules to improve thermochemical parameters.
- To investigate macroscopic systems such as flame dynamics in order to develop more precise models for real combustion systems.

Anticipated benefits to the program in particular are to provide a predictive understanding of combustion systems and a deepened understanding of chemical physics in general.

FY 2014 HIGHLIGHTS

A chemical reactor to probe unimolecular and bimolecular chemical reactions under combustion relevant conditions was developed. By probing the reactions of hydrocarbon free radicals (phenyl) with acetylene under combustion-like conditions by synchrotron based photoionization mass spectrometry, the very first direct experimental evidence for a combustion mechanism proposed over 30 years ago, but never observed, is reported. In another set of experiments, a complete identification of the reaction of the phenyl radical with molecular oxygen, which plays a central role in the degradation of poly- and mono- cyclic aromatic radicals in combustion systems was completed. Mechanistic insight into pyrolysis of biofuel compounds (dimethyl furan, cyclopentadienone, & benzyl radical) was obtained using the high temperature chemical reactor. A miniature shock tube & jet stirred reactor was interfaced to synchrotron radiation and results obtained for high temperature and pressure systems. Two dimensional gas phase chromatography with VUV photoionization mass spectrometry has revealed new details about complex hydrocarbon samples (fuel) as well as isomer level product distributions of

heterogeneous oxidation reactions. The viability of the technique was demonstrated for the analysis of diesel fuel, a prototypical environmental pollutant whose chemical complexity itself is a stringent test of any new analytical technique. Insights into the influence of molecular structure and thermodynamic phase on chemical mechanisms are obtained by identifying products of the OH-initiated oxidation of submicron particles composed of either n-octacosane (a linear alkane) or squalane (a highly branched alkane). Experimental investigations of soot precursors and incipient particle characteristics with the development of a predictive model for the chemical composition of soot nanoparticles was completed.

Gas-Phase Molecular Dynamics

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PROGRAM SCOPE

Members of the Gas Phase Molecular Dynamics group develop and apply high resolution spectroscopic and quantum theoretic tools to study the structure, dynamics and chemical reactivity of molecular species relevant to hydrocarbon combustion. Our overlapping interest and expertise in spectroscopy, dynamics, theory, and kinetics allow collaborative approaches to frontier topics in chemical physics. Current interests include studies of the collisional dynamics of CN radicals, understanding the relationship between collisional energy transfer processes and observed spectroscopic line shapes, and modeling of fast chemical reactions using *ab initio* potential energy surfaces computed on the fly. High resolution spectroscopic measurements of sub-Doppler molecular spectra provide both insights into electronic wavefunctions through the hyperfine interaction, as well as precision frequencies for the analysis of complex, overlapping spectra. New work includes the development of efficient algorithms for full-dimensional calculations of anharmonic vibrational levels of polyatomic free radicals as a guide to new spectroscopic measurements, the development of very precise and accurate methods for line shape and position measurements and new optical double resonance methods for sub-Doppler collisional energy and momentum transfer measurements in free radicals.

FY 2014 HIGHLIGHTS

High resolution saturation spectroscopy of free radicals A collinear sub-Doppler double-resonance method has been developed to measure the pattern of energy splitting of nuclear spin states in reactive radicals. By frequency locking a tunable sideband of one laser to an optical cavity, which in turn is frequency locked to a second laser, we have implemented a scheme to record velocity-tagged and probed optical transitions in the near infrared region with linewidths of 2-3 MHz and splitting patterns that can be measured with typical errors of 0.5 MHz for radicals that last for a fraction of a millisecond in a room temperature gas cell. Efficient algorithm for calculating molecular resonance energies, lifetimes and wavefunctions A resonance state is a configuration of atoms with too much total energy to exist as a stable molecule, but possessing a specific energy and configuration that may make it persist for longer than a molecular vibrational period, and play a subtle role in collisions important in energy transfer and chemical reactions. We have developed a general and problem-independent algorithm to efficiently

calculate all bound and hundreds of the lowest-lying resonance states of molecules. The method produces not only the energies and lifetimes, but also the wavefunctions, if desired. The algorithm has been developed using a complex guided spectral transform Lanczos approach, where the transform spectral functional is expanded in a series of complex formal orthogonal Lanczos polynomials. The algorithm has been demonstrated on resonance states of HO₂, where resonances can influence the chain branching reaction of H + O₂ to give O + OH or be stabilized to form HO₂. Sub-Doppler frequency-comb referenced measurements in acetylene hot bands Doppler-free transition frequencies for hot bands involving the lowest two vibrational fundamental vibrations have been measured in the symmetric + antisymmetric stretching combination band of acetylene.

Gas-Phase Chemical Physics (Experiment and Theory)

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Funding: \$1,728,000 (2014)

PROGRAM SCOPE

The objectives of these programs are to develop the basic knowledge and understanding of the mechanisms and dynamics of elementary chemical reactions that have a major impact on combustion and advanced energy production technologies. Recent emphasis has been to determine the structure and photochemical reaction dynamics of free radicals, unusual transient species, heterogeneous chemistry, and highly-excited polyatomic molecules, and to provide microscopic details of primary dissociation and bimolecular processes. These objectives are achieved with a strongly-coupled experimental and theoretical computational approach, using emerging technologies. Experimental dynamics studies use advanced molecular beam and laser techniques, photofragmentation translational spectroscopy, and ion and electron imaging. Kinetics studies involve heterogeneous dynamics, mass-selective product detection and UV-VUV synchrotron and laser spectroscopy, and coherent dynamics. New theoretical methods and models are developed both to provide insight into chemical reactivity and the dynamics of reactive processes and also to develop methods to carry out forefront calculations to guide and model these experimental studies. Studies taking advantage of the chemical dynamics beamline comprise multiple molecular beam machines, aerosol equipment, and high resolution monochromators in the vacuum ultraviolet spectrum, in conjunction with a range of commercial laser systems and associated resources. A new initiative incorporates nano-imaging of materials with chemically specific synchrotron detection. This beamline, providing the world's brightest source of continuously-tunable vacuum ultraviolet light, is a National User Facility initiating a new era in the study of primary photochemistry, spectroscopy, photoionization processes and reaction dynamics.

FY 2014 HIGHLIGHTS

Using a multiplexed photoionization mass spectrometer at the ALS, formation of fulvene in the reaction of C₂H with 1,3-butadiene was observed, and the reactive potential energy surface was studied

computationally. Low temperature combustion product species were analyzed with tunable-synchrotron photoionization spectroscopy in a collaborative study relevant to the Korcek mechanism of decomposition of intermediate ketohydroperoxide species into acid, ketone and aldehyde pairs. Using the fast reactive beam instrument, ozone photodissociation was studied at 193 and 157nm. Particularly at the shorter wavelength, the data corresponds to equal energy partitioning in two of the recoiling O atoms, consistent with a synchronous concerted mechanism in which the two O-O bonds in ozone dissociate symmetrically at the same time. Phenyl photodissociation at 193 nm was reinvestigated to explore whether acetylene loss occurs statistically or is directed via conical intersections. Carefully controlling reaction conditions to keep the radicals cold and minimize 2-photon processes leads to branching between the two channels consistent with statistical ground state dissociation. With regard to understanding reaction dynamics of aerosols, the reaction of iodine atoms with submicrometer squalane and squalene droplets was studied. A number of significant theoretical developments were accomplished, including development of a new density functional, omegaB97X-V, which was designed by a novel survival of the most transferable approach, and outperforms all existing functionals tested for accuracy in intermolecular interactions. Additionally, the recently developed attenuated MP2 method was improved to attain greater accuracy for thermochemistry in finite basis sets, by spin-component scaling. A new semi-classical approach to non-adiabatic dynamics, based on an Ehrenfest approach with a novel binning procedure, showed accuracy as well as efficiency in tests on pilot systems.

An Expert *Ab Initio* Transition-State-Based Master Equation Code

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Funding: \$248,000 (2014)

PROGRAM SCOPE

The *ab initio* transition-state-theory-based master equation (AITSTME) approach has proven to be an extremely useful procedure for predicting the rate coefficients of gas phase chemical reactions. Such calculations consist of four components: (1) electronic structure calculations of the potential energy surface, (2) microcanonical TST calculations, (3) a model for energy transfer, and (4) the solution of the master equation representing the time dependence of the energy resolved populations. Current software implementations of the AITSTME approaches have various limitations that constrain their utility in several aspects. This project is developing a new state-of-the-art, open-source, user-friendly AITSTME software package that incorporates recent theoretical advances. A modular framework will facilitate continued development and couplings to other codes. This AITSTME code will allow for the routine prediction of multiwell, multichannel thermal rate coefficients at the highest levels of accuracy. Correspondingly, it would contribute to the continued increase in the fidelity of chemical models for combustion and thus to the predictive simulation of internal combustion engines. The overall goal of the project is to provide a code that plays the same role in the prediction of rate coefficients for elementary reactions that CHEMKIN plays in chemical kinetic modeling.

FY 2014 HIGHLIGHTS

The main goal of AITSTME is the development of a suite of integrated codes for accurately predicting elementary kinetics. A new method and code, One-Dimensional Minimizations (1DMIN), for predicting transport, and newly modified codes and methods for accurate calculations of energy transfer, Direct Nonadiabatic Trajectories (DiNT), are available and being used in the larger scientific community.

High Pressure Combustion Chemistry: From Fundamentals to Accurate Models

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Funding: \$1,067,000 (2014)

PROGRAM SCOPE

The goal of this project is to explore the fundamental effects of high pressure on the chemical kinetics of combustion and to use that knowledge in the development of accurate models for combustion chemistry at the high pressures of current and future engines. We design and implement novel experiments, theory, and modeling to probe high-pressure combustion kinetics from elementary reactions, to submechanisms, to flames. The work focuses on integrating modeling, experiment, and theory (MET) through feedback loops at all levels of chemical complexity. We are currently developing and testing the methodology for propane, small alcohols, and dimethyl ether as key prototype fuels. The consortium expands and enhances collaborations between Argonne's Dynamics in the Gas Phase Group and the Combustion Chemistry Group in Sandia's Combustion Research Facility.

FY 2014 HIGHLIGHTS

We have made considerable progress in applying the MET paradigm to propane combustion, to the development of mechanisms for small oxygenated hydrocarbons, and of a core mechanism. Synchrotron based multiplexed photoionization mass spectrometry studies of Cl initiated propyl oxidation chemistry have been performed and the data has been employed in a novel multiscale modeling approach. Studies exploring non-thermal effects for propane oxidation were published. High pressure rate measurements were made for OH + alkene reactions. We recently detected ketohydroperoxide (KHP), an important product of QOOH + O₂ reactions, in butane oxidation at pressures up to 2 atm. A high repetition rate shock tube has been developed and tested at both the Advanced Light Source at Berkeley and the Advance Photon Source at Argonne. Preliminary results were obtained for dimethyl ether decomposition. The reflected shock tube technique with H-ARAS detection was used to study the

reactions of CH₃ radicals with C₂H₆, C₂H₄, and C₂H₂ over the T-range 1100-1350 K. Measurements of H/D-atoms that result from shock heating mixtures of CH₃OH and tert-butylhydroperoxide (as a thermal source for OH) were used to probe the kinetics of OH + CH₃OD/CD₃OH. Modeling efforts suggest an important role for direct decomposition of the initially formed radicals. A long-term project developing a high accuracy core mechanism is nearing completion. This mechanism will include our emerging understanding for low-temperature propane oxidation and of non-thermal Boltzmann effects.

Combustion Research Facility

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Funding: \$9,831,000 (2014)

PROGRAM SCOPE

This work proposal covers fundamental combustion research being conducted in the Combustion Research Facility (CRF) at Sandia National Laboratories, Livermore, CA. This research attacks challenging scientific issues that are crucial to a better understanding of combustion phenomena. In experimental studies, emphasis is on the development and application of advanced, laser-based detection technologies. In chemistry, studies include chemical dynamics, chemical kinetics, flame chemistry and combustion modeling. In diagnostics, emphasis is given to development and application of spatially and temporally precise, non-perturbing methods that provide chemical or gas-dynamical information, and that are applicable in harsh combustion environments. Theoretical efforts range from basic molecular structure calculations to quantitative simulations of diagnostic signals to detailed modeling of multicomponent, chemically reacting turbulent flows. Research activities emphasize the examination of fundamental gas-phase reaction and fluid dynamic processes in controlled combustion environments. Projects include experimental and numerical studies of premixed and non-premixed flames in both laminar and turbulent flow. Theoretical efforts are directed at the modeling of multicomponent reacting flows. Experiment and theory are closely coupled as new thrusts are designed. The overall long-term goal is to provide sufficient fundamental understanding of reaction and fluid dynamics processes in combustion to arrive at detailed predictive, physical models of practical combustion systems. This research program serves three key functions. First, it provides critical expertise in the fundamental

sciences of combustion; second, it provides information and new technologies that directly impact applied research combustion efforts; and third, it attracts scientists to the CRF to participate in ongoing research and to share in technological advances.

FY 2014 HIGHLIGHTS

Diagnostic developments allow broader & less intrusive measurements of key combustion properties. We invented a new 2D hyperspectral coherent anti-Stokes Raman spectroscopy technique, allowing single-shot, spatially resolved detection of multiple species & temperature. Varying soot properties in different regions of a flame suggest that *in situ* optical diagnostics can infer composition without extraction. We developed a polarization-separation Raman spectroscopy line imaging system that enables virtually interference-free spectroscopy in fuel-rich flames. We performed the first high-speed tomographic particle image velocimetry measurements, providing new insight into flame extinction & re-ignition. Chemical reaction and transport computations have become more efficient & accurate. Stationary points on the C_3H_5O potential energy surface have been fully characterized by an automated method. We used classical trajectories and *ab initio*-based force fields to yield first-principles diffusion coefficients accurate to within 2%. Synchrotron photoionization probe details of combustion mechanisms. Carbonyl oxide reactions with organic acids were remarkably rapid, near the gas-kinetic collision limit. Isomer-resolved measurements in 1-hexene flames showed that benzene is formed via a fulvene intermediate. We characterized initial oxidation reactions using time-resolved & isomer-specific product concentrations from the pulsed-photolytic Cl-initiated oxidation of n-butanol. A new density-weighted analysis of the direct numerical simulation of a premixed turbulent flame demonstrated a 'diffusive-reactive' range of small scales. We determined the effect of uncertainty in chemical reaction rates on flame ignition using a novel intrusive uncertainty quantification technique that remained stable in highly nonlinear computations. The first non-equilibrium theory of two-phase interfaces under trans-critical conditions was developed & applied to high-pressure fuel injection.

Chemical Composition of Soot Nanoparticles

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Funding: \$139,000 (2014)

PROGRAM SCOPE

The goal of this program is to develop a comprehensive and predictive computer code for the chemical composition of nanoparticles produced in diffusion and premixed flames. To this end, a new generation of the multiscale AMPI code will be developed to describe the formation of soot nanoparticles as a combination of chemical and physical reaction pathways for various fuels. This development will require close collaboration between modeling and state-of-the-art experimental techniques that will guide and validate the model. This FWP includes the experimental studies that will be conducted at Sandia National Laboratories and the Advanced Light Source (ALS) to provide a rigorous basis to guide the modeling efforts at the University of Michigan. The underlying combustion chemistry of target fuels will be investigated using flame sampling molecular-beam mass spectrometry employing single-photon and resonantly enhanced multi-photon schemes. A counterflow burner will be built to provide a better

platform for controlling flame conditions. To follow the kinetics of soot particle inception and growth, we will use an online particle sampling technique followed by measurements of particle size distribution functions using a scanning mobility particle sizer. The chemical composition of soot nanoparticles will be characterized using aerosol mass spectrometry at the ALS. These results will be directly compared with the data obtained from the new version of the AMPI code developed at University of Michigan.

FY 2014 HIGHLIGHTS

Measurements of isomeric distributions of soot precursors suggest that soot formation may involve isomers of polycyclic aromatic hydrocarbons beyond the most thermodynamically stable species, contrary to traditional assumptions.

Chemical Dynamics in the Gas Phase

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Funding: \$4,099,000 (2014)

PROGRAM SCOPE

Our goal is to develop an understanding of the chemical reactions, energy transfer processes, and coupled kinetics processes involved in combustion. This effort will ultimately provide the foundation for predictive combustion modeling. Our approach combines a theoretical effort in the energetics, dynamics, and kinetics of chemical reactions with an experimental effort in thermochemistry, dynamics, and kinetics under both chemically isolated conditions and the more complex conditions of flames and engines. The effort is split ~50/50 into theory and experiment. The theoretical effort embraces both applications of existing theoretical methods and the development of new theoretical methods. Electronic structure techniques that determine intermolecular forces, dynamics techniques that determine molecular responses to these forces, and kinetics techniques to determine the rates of the resulting reactions are all being pursued. Simulations of more complex combustion environments involving coupled kinetics and transport are being developed, along with approaches for uncertainty analysis and sensitivity analysis. The experimental effort encompasses state-resolved measurements at low temperatures, thermal reaction kinetics measurements at high temperatures, and photoionization and photodissociation measurements of thresholds and state-resolved product distributions. Reaction rates, branching ratios, product distributions, the effect of initial vibrational excitation on reactivity, and ion-cycles for thermochemical information are all being examined. Both the theoretical and experimental components of the program are vertically integrated to span the range of phenomena relevant to the study of chemical reactivity. The group's greatest asset is the synergy that results from

the strong interaction between the theoretical and experimental efforts. The group's work is designed to provide a fundamental understanding of both major and trace reactions of importance in combustion.

FY 2014 HIGHLIGHTS

Over the past year, we have performed new experimental and theoretical studies addressing a wide range of problems relevant to the thermochemistry, dynamics, kinetics, and modeling of combustion processes. A few highlights from the past year are mentioned here. (1) A new version of the Active Thermochemical Tables (ATcT) was released (see the website: www.atct.anl.gov) providing accurate thermochemistry for nearly 1000 species of relevance in combustion. (2) A combined experimental and theoretical study of abstraction reactions involving OH and methanol or propane revealed that the product radicals can be very 'hot' (internally excited). These hot radicals can have a significant effect on subsequent reactions, and the general implications of this phenomenon are now being explored. (3) A new miniature shock tube for high-temperature studies of combustion chemistry was tested at both the Advanced Photon Source and the Advanced Light Source. The portable nature of this device is unique, and will allow many powerful tools based on x-rays and vacuum-ultraviolet light to be applied to shock-tube experiments for the first time. Such studies should provide new insight into high-temperature chemistry, as well as into processes such as soot and particle formation. (4) An approach for performing sparse global sensitivity analysis (GSA) was developed that greatly reduces the number of simulations required to achieve accurate results. This advance has allowed GSA for problems that previously would have required intractable computational resources. For example, sparse GSA was applied to the combustion of an n-heptane/methyl butanoate blend in a compression ignition engine, allowing the identification of key sensitive reactions and, ultimately, the improvement of the simulations. The approach can be applied not only to the chemistry, but also to the investigation of sensitivities to other engine parameters.

Geosciences

Institutions Receiving Grants

Adsorption Equilibrium and Kinetics at the Goethite-Water Interface

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PROGRAM SCOPE

We are developing an approach for metal surface complex prediction to predict adsorption behavior. We combine the use of several techniques including bulk adsorption experiments, X-ray absorption, infrared, total internal reflection Raman, and vibrational sum frequency generation (XAS, IR, TIR-Raman, VSFG) spectroscopies, and molecular modeling to investigate ion adsorption at mineral surfaces. XAS and TIR-Raman provides data on how the metal binds to the surface (e.g., monodentate, bidentate), IR provides data on bulk anion adsorption at mineral surfaces from aqueous solutions, and VSFG provides surface specific data on anion adsorption at the mineral surface as well as impact of adsorbed metal-anion pairs on water structure at the mineral surface. Molecular modeling is used to guide spectroscopic data interpretation by providing information on water structure around ions in solution and the structure of metal-anion complexes in aqueous solutions. In addition, molecular modeling is used to provide insight into water structure at mineral surfaces, the surface sites involved in ion adsorption, and the distribution of ion pairs between aqueous solution and the mineral surface. Our studies have focused on systems involving alkaline earth metal (Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+}) and heavy metal (Co^{2+} , Cd^{2+}) cations. The anions we have selected for study include Cl^- , NO_3^- , ClO_4^- , SO_4^{2-} , SeO_3^{2-} , and SeO_4^{2-} . Ion adsorption and the potential formation of ternary complexes on silica (quartz, amorphous silica), alumina (corundum and gibbsite), and ferric iron oxides (goethite and hematite) are under investigation.

FY 2014 HIGHLIGHTS

Research taking place in the Allen Lab of Ohio State has primarily been focused on using TIR-Raman spectroscopy for the investigation of (1) the effects of adsorption of simple oxyanions (ClO_4^- , NO_3^- , SO_4^{2-}) on the interfacial pH at the aqueous/silica (SiO_2) interface, and (2) the selenium oxyanions (SeO_3^{2-} , SeO_4^{2-}) adsorption to silica and ferric iron oxides (e.g., hematite ($\alpha-Fe_2O_3$)), two common mineral oxides relevant to geochemistry. TIR-Raman spectroscopy is analogous to attenuated total reflection infrared (ATR-IR) spectroscopy in that it uses the evanescent electric field generated under the TIR condition to probe the mineral/aqueous interface. The evanescent field scatters by interacting with ions bound to mineral surface groups and dissolved in the bulk. In comparison to ATR-IR, TIR-Raman spectroscopy has the advantage of increased surface specificity as the probing depth of the evanescent field in the aqueous phase at visible wavelengths (400–800 nm) will be 200–400 nm. The adsorption of geochemically relevant oxyanions (perchlorate (ClO_4^-), nitrate (NO_3^-), and sulfate (SO_4^{2-})) on the interfacial pH of the silica/aqueous interface was investigated. As the adsorption at the charged silica/aqueous interface is characterized by the protonation of oxyanions, these results suggest that they

have different abilities to modify the silica surface as their affinities for protonation are different in the interfacial region. By applying the Henderson-Hasselbach model and using the areas of the peaks associated with the deprotonated and protonated oxyanion species, we estimate the interfacial pH at the silica/aqueous interface for each oxyanion solution: SO_4^{2-} (3.2 ± 0.6) > ClO_4^- (0.0 ± 0.3) \sim NO_3^- (-0.2 ± 0.1), which differs significantly from the bulk pH (2.0 ± 0.2). This result suggests that nitrate and perchlorate oxyanions tend to modify the silica surface to be more positively charged, whereas sulfates leave it relatively neutral.

Towards a Predictive Thermodynamic Model of Oxidation States of Uranium Incorporated in Fe(Hydr)Oxides: the Role of Coordination Environments and Charge Compensation Mechanisms

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PROGRAM SCOPE

The overall objective of the joint efforts with the collaborators at PNNL is to understand the role of the U environment, including its coordination, on the reduction of U(VI) to U(V) and U(IV) at the ferrous mineral-fluid interface. Key experimental techniques used include x-ray photoemission spectroscopy, XPS, and x-ray adsorption near edge structure, XANES. The theoretical efforts summarized here are directed toward understanding the chemical interactions from the analysis of these core-level spectra. These efforts have had substantial recognition and impact. The review describing how XPS can give insights into materials properties published by Bagus, Ilton, and Nelin in Surface Science Reports in 2013 continues to be among the 25 most downloaded papers. While the initial efforts have involved the theoretical interpretation of XPS; the focus has been extended to stress XANES. We expect to extract a wealth of geochemical information because the methods we use take full account of the contributions to the XANES of multiplets, intermediate coupling, and covalent mixing. The scope of the theoretical efforts is twofold. (1) To improve the theoretical and computational capabilities for the electronic structure of initial and core-excited states, especially for many-body effects. And, (2) to apply these unique theoretical capabilities to resolve key issues for U and for ferrous minerals. In this period, there have been computational breakthroughs that have allowed us to treat more complex and more realistic models of geochemical systems. These have included a new diagonalization program faster by over a factor of 6 to allow including the additional many-body effects needed to more accurately describe XPS satellites. We have also extended our ability to determine XANES intensities so that we could study distorted octahedral models of UO_x ; see highlights. Further enhancements planned for FY 2015 will give capabilities to treat the XPS and XANES for complex species.

FY 2014 HIGHLIGHTS

New methods developed to accurately characterize the extent of covalent mixings in heavy metal oxides and to determine how core-level spectra reflect this chemical bonding were reported. An important feature of this methodology is that, for the first time, estimates can be made of the uncertainty in the assignment of effective charges. The essence is that the number of electrons to be assigned to anions and cations are determined separately by projection of sub-unit orbitals without, as is normally done,

imposing the constraint that the total number of electrons be fixed. The deviation of the gain in cation charge and the loss of anion charge from equality is a direct measure of the uncertainty of the assignment. Two important results for XPS have been found. First, there is substantial covalent character, especially for heavier, lanthanide and actinide, cations and, second, the closed shell screening, a concept first introduced by Bagus and Ilton, is much more important than expected. This methodology has been applied to XANES. The analysis of XANES with Ilton, PNNL, was initiated to study how the broadening of deep edge U XANES depends on the U oxidation state. The broadening was explained by the different covalent mixing for different oxidation states. This initial work has been extended in FY2014. The NEXAFS for distorted crystal geometries has a direct relationship to covalency. The role of embedding of the local cluster for UO_x has been examined using methods developed for simpler MgO. More realistic embeddings have led to differences in the XANES; work will be continued in FY 2015. Studies of the Fe 2p XANES edges have been initiated with the goals of understanding the sensitivity to XANES to Fe charge state and to the environment. New effects, not key in UO_x , are multiplet splitting and intermediate angular momentum coupling, which can bring a dramatic richness to the XANES. The promising initial results will be investigated further in FY 2015.

Aqueous Geochemistry at High Pressures and Temperatures

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PROGRAM SCOPE

This project is aimed at experimental characterization of the physical nature of aqueous solutions and carbon dioxide at extreme pressure and temperature conditions relevant to processes occurring in the interior of the Earth. Research in this area has long been limited by the extreme experimental challenges and lack of data under the appropriate conditions. The vast majority of studies of aqueous geochemistry relevant to terrestrial problems of fluid-rock interactions have been conducted at 0.3 GPa or less, and the widely used Helgeson-Kirkham-Flowers equation of state for aqueous species is applicable only at $\sim < 0.5$ GPa. These limits are unfortunate because fluid flow and reactions plays a central role in many deeper environments. Recent efforts including our own, have resulted in new experimental techniques that now make it possible to investigate properties of homogeneous and heterogeneous equilibria involving aqueous species and minerals over a much broader range of pressure and temperature appropriate for deep crustal and upper mantle processes involving water-rich fluids. We are carrying out 1) Brillouin scattering measurements of the equations of state and molar volume of water and carbon dioxide to over 10 GPa and 870K using precise resistance heating of samples under pressure in the diamond anvil cell, and 2) the phase diagrams of the water and CO_2 , and 3) Exploring new experimental approaches to measurements of sound velocities, EOS, and phase relations by Brillouin scattering to far greater pressures and temperatures.

FY 2014 HIGHLIGHTS

Our earlier work revealed that there are significant differences in the equation of state (EOS) and especially the phase diagrams of water, depending on the experimental details of resistance heating

experiments using the diamond anvil cell. New experimental approaches are needed to accurately determine the EOS and phase relations of water and related substances at extreme pressure-temperature conditions. Our most recent highlights include: 1) Development of new gas pressure membrane diamond cells for fine and accurate control of pressure; 2) Determination of the elastic properties and EOS parameters of solid carbon dioxide by Brillouin scattering measurements at high pressure across the CO₂ I-III phase transition at ~10 GPa. Our results are in agreement with recent synchrotron X-ray diffraction measurements of the I-III transition, and Raman measurements of a high-pressure electronic transition in CO₂; 3) Development of a new apparatus for Brillouin scattering sound velocity and EOS measurements at ultra-high pressure-temperature conditions. With this new system, heating of pressurized samples in the diamond cell is achieved via a carbon dioxide laser. Initial Brillouin scattering measurements were successfully made on liquid water to temperatures of 2500K, greatly exceeding the P-T limits of previous measurements using resistance heating. This experimental advance will allow a new generation of measurements of the properties and phase relations of water and other materials under pressure-temperature conditions that were previously unattainable.

Deformation and Fracture Properties of Shale at Nanoscale

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PROGRAM SCOPE

Shale is a fine-grained sedimentary rock composed of clay and organic materials forming a heterogeneous matrix or composite. Shales are often rich in unconventional oil and natural gas, but their low permeability makes the extraction of this energy resource difficult. The permeability of shales can be increased by hydraulic fracturing, a technique that paved the way for most of the several giant natural gas fields now in operation. The deformation and fracture properties of shales depend on the mechanical properties of their basic constituents, including the solid clay particles and the nanoscale porosity forming the porous clay composite. A great deal of understanding of the overall mechanical properties of shales can be gained by studying the deformation and fracture properties of these constituents. This project will build upon our recently acquired ability to image (using FIB-SEM) the 3D geometry of a porous shale sample to nanometer resolution, as well as test this sample on a nanoindenter at both the particle and (sub-micron) composite scales, to develop a 3D mechanistic model that will interpret the results of nanoindentation tests. We will use the finite element method to model the clay particle as well as the shale composite. We will capture the effects of the elasticity of the particle, plastic yielding, and damage induced by the indenter, including the fracturing and chipping within the mineral grains and around the perimeter of the indent. We will use an enhanced finite element formulation based on the assumed enhanced strain finite element method to capture damage emanating from the indentation tests.

FY 2014 HIGHLIGHTS

Nanoindentation tests, spanning various length scales ranging from 200 nanometers to 5 micrometers deep, were performed on a sample of organic-rich Woodford shale in both the bedding plane normal

and bedding plane parallel directions. Focused ion beam milling (FIB), scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDX) were utilized to characterize the shale at the scale of the nanoindentation testing as being comprised predominantly of clay and other silicate minerals suspended in a mixed organic/clay matrix. The nanoindentation tests reveal the mechanical properties of the relatively homogeneous constituent materials as well as those of the highly heterogeneous composite material. Loads on the order of a few milliNewtons produced shallower indents and demonstrated the elastic-plastic deformation response of the constituent materials, whereas higher loads of as much as a few hundred milliNewtons produced deeper indents revealing the response of the composite matrix. In both cases, significant creep was observed. We use nonlinear finite element modeling utilizing an isotropic critical state theory with creep to capture the indentation response by calibrating plastic material parameters to the laboratory measurements. The simulations provide a means of extracting plastic material parameters from the nanoindentation measurements, and reveal the capabilities as well as limitations of an isotropic model in capturing the response of an inherently anisotropic material. The results are reported in a recently published paper: Bennett, K.C., Berla, L.A., Nix, W.D., Borja, R.I. (2015). Instrumented nanoindentation and 3D mechanistic modeling of a shale at multiple scales, *Acta Geotechnica*, DOI:10.1007/s11440-014-0363-7.

Computational and Experimental Investigations of the Molecular Scale Structure and Dynamics of Geologically Important Fluids and Mineral-Fluid Interfaces

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Funding: \$28,551 (2014)

PROGRAM SCOPE

Research supported by this grant and the closely linked DE-FG02-08ER15929 (R.J. Kirkpatrick, PI, Michigan State University) focuses on addressing fundamental scientific questions regarding the structure, dynamics, and reactivity of geochemically important fluids, fluid-mineral interfaces, and confined fluids on a molecular scale using a combination of computational molecular modeling and spectroscopic methods, primarily nuclear magnetic resonance (NMR) spectroscopy. The Bowers group handles the wet chemistry, much of the basic sample characterization, and drives a majority of the NMR spectroscopic investigations. The Kirkpatrick group is responsible for the computational modeling and part of the NMR experiments. Collaboration between the two groups is very close, with computational modeling motivating our spectroscopic studies and spectroscopic results helping to identify key questions for computational modeling. The combination of computational and spectroscopic approaches is highly effective in addressing otherwise intractable molecular-scale problems concerning the fundamental physical and chemical behavior of fluids and interfaces, which are central to understanding such geological problems as the migration of chemicals in soil, sediments, and rocks, and the processes by which fluids alter sediment and rocks. The objectives during this grant period focus specifically on developing a deeper understanding of molecular-scale structure and dynamics in smectite-natural organic matter (NOM) composite materials that are ubiquitous in the soils, sediments, and many sedimentary rocks. We are providing key new insights into how NOM, a key sink for many inorganic and organic contaminants, influences the binding and dynamics of cations, aqueous fluids, and

supercritical CO₂ in the composites; the binding structures and mechanisms of NOM-mineral association under a variety of geochemical conditions; and how NOM influences the physics of composite hydration.

FY 2014 HIGHLIGHTS

Our work focused principally on understanding how pH, charge-balancing cation (CBC), and solution ionic strength influence the structures and molecular-scale ion and fluid behaviors in pure flocculated NOM and in hectorite (a trioctahedral smectite)-Suwannee River NOM composites. Helium-ion microscopy (HeIM) and X-ray diffraction (XRD) reveal a variety of morphologies in flocculated NOM depending on the ionic strength of the preparatory solution, pH, and CBC present. In contrast, HeIM and XRD show that homogeneous composites of hectorite and NOM form at pH 12 independent of the ionic strength and CBC. We also find that the NOM-rich features in composites examined last year have identical morphologies to pure flocculated NOM. The composite hydration physics reflect the hydration behavior of the base hectorites, with NOM exerting a minor influence on composite retention of 2H₂O when exposed to a dry atmosphere. Associated NMR experiments show similar cation coordination behavior and dynamics as the base clays, suggesting that most Cs⁺, K⁺, Na⁺, and Ca²⁺ remain associated with the smectite and mobile regardless of pH, ionic strength, or presence of NOM. However, subtle variations in the NMR results indicate some influence of NOM on the cation coordination environment. Related computational studies are in progress at MSU. Composites equilibrated at 43% RH and exposed to supercritical CO₂ (scCO₂) at conditions relevant to geological CO₂ sequestration show that the ¹³³Cs chemical shift is highly influenced by the presence of both NOM and scCO₂, but that the MHz-scale dynamics are unaffected (unlike Na-hectorite composites). In contrast, the ⁴³Ca NMR results are not influenced significantly by NOM or scCO₂, suggesting little direct interaction with Ca²⁺. We observe no evidence of carbonate mineral formation in any composite exposed to scCO₂ to date. Again, molecular modeling is beginning to shed new light on these results (see highlights in DE-FG02-08ER15929).

An Investigation of Roughness and Weathering at the Bedrock-Regolith Interface

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Funding: \$600,000 (2014-2017)

PROGRAM SCOPE

Research funded by the Department of Energy Office of Basic Energy Science aims to develop understanding of geological systems that are important to our national well-being. For example, to understand the evolution of nuclear waste repositories or hydraulically fractured rocks requires projections of the evolution of rock-water systems forward in time. The geochemical community has developed the capability to provide numerical simulations of rock-water systems but often the underlying conceptual models are not adequate descriptors of the natural systems or the appropriate parameterizations for model phenomena are lacking. In this DOE-OBES project, conceptual models are tested for the most well studied examples of geochemically evolving systems found at earth's surface: weathering rocks. The approach incorporates numerical modelling and field measurements of different rocks in different climates at different spatial scales. Researchers in this project are testing this conceptual model: rocks start as fractured porous materials which increasingly break into smaller

fragments during weathering. Inside the fragments, reactants move to mineral grain surfaces by diffusion, but in the soils surrounding the fragments, advection dominates transport. To parameterize models for a few targeted weathering systems, depth profiles are being measured for these reactants: i) the mineral-water interface; ii) CO₂, the main weathering acid; and iii) O₂, the ultimate electron acceptor. The project incorporates i) analyses of strategically-chosen regolith profiles developed on ridgetops and hillslopes; ii) measurements of O₂ and CO₂ in boreholes on crystalline and shale rock; iii) an investigation to determine if oxidation causes fracturing in cores of granite and diabase; and iv) a study targeting how O₂ and CO₂ affect deep weathering of a rock type that can be considered as “pre-fractured” – shale. With these efforts, deeper understanding of weathering systems is emerging.

FY 2014 HIGHLIGHTS

We are planning to complete neutron scattering on regolith developed on PA diabase and on new regolith profiles we will sample on ultramafic rocks. We have gathered samples of the diabase; to sample ultramafics we are planning to drill in summer 2015. We have been developing a collaboration with Beth Parker and John Cherry at Univ of Guelph (Canada) as we learn to use their i) back pack core drill; ii) Winkie drill; and iii) Hydra drill. We have continued to monitor our boreholes in Virginia and Pennsylvania that are instrumented with soil gas sensors. We are currently writing up these results for publication in summary form and are developing a second paper describing temporal variations in gas–depth data with more specifics. L. Anovitz at Oak Ridge National Laboratory has heated granite core samples with selenious acid to manufacture samples that show increasing oxidation of the ferrous iron. The high temperatures and acid concentrations used in our initial experiment were chosen to maximize oxidation. These samples have been cored and are being prepared for chemical analysis and neutron scattering. We are now gathering samples of shale for analysis of nano-porosity as a function of depth. We target shales from two well-characterized sites: (1) the Rose Hill shale in central PA, (2) the Yager terrain shale in the Eel River Critical Zone Observatory, in the coastal range of northern California. Neutron scattering on other shales from depth or from weathering systems (Marcellus and Rose Hill Formations) is also ongoing. Finally, we continue to test the idea that the weathering advance rate depends on the curvature and roughness of the reaction front: specifically, the thickness and depth of the bedrock/regolith interface is larger where curvature is larger.

Pathways for Oxygen-Isotope Exchanges in Nanometer-Size Aqueous Clusters

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Funding: \$140,413 (2014)

PROGRAM SCOPE

The project employs isotope-exchange methods and spectroscopy to elucidate mechanisms of reactions affecting oxide ions in water. The work is now focused on extending NMR spectroscopy to pressures of up to 20 kbars. High pressures are useful for detailing changes in coordination and solvation in reaction mechanisms. We have invented such an NMR probe and use it to measure activation volumes for isotope-exchange reactions and changes in molecular conformations in aqueous solutions.

FY 2014 HIGHLIGHTS

The major accomplishment this year was the publication of the inaugural paper on NMR spectroscopy to 20 kbars, which was identified as a 'Very Important Paper' by the journal *Angewandte Chemie* and used as a cover figure. DOI: 10.1002/anie.201404994. In this work we extended by at least a factor of two the pressure range over which NMR spectroscopy can be accomplished on aqueous solutions. We ran experiments to such pressures that not only the volume of reaction, but also the compressibility of the reaction, were measurable. It was a stunning advance to the field of reaction mechanisms in aqueous reaction kinetics. This NMR probe is now being used to extend the measurements of T1 (longitudinal relaxation) of D₂O and ¹³⁹LaCl₃ solutions in order to demonstrate our bone fides to the community. We have matched the work of Jonas at lower pressures and extended it to 1.6 GPa. These measurements are important to geochemists because the influence of changes in the solution dielectric constant diminish beyond about 0.8 GPa and the intrinsic reaction volumes and compressibilities can be measured at pressures beyond this point, which contributes directly to geochemical theories of electrolyte solutions at high pressures. Because of recent extension of the dielectric constant of water to 6.0 GPa via simulation, new methods of verifying the predictions are needed. With this technology, we can measure reaction volumes and speciation directly and simply at pressures of up to 2.0 GPa in aqueous solutions. A second advance is by the research team. We have designed and built a high-pressure NMR probe that allows simultaneous measurements of ¹H and ¹³C NMR spectra at pressures of up to 2.0 GPa in aqueous solutions. The design and fabrication is complete and we are now testing it. The design is easily adapted to spectroscopies beyond NMR. Several other publications were also accepted during the funding period, but nothing as spectacular as the *Angewandte Chemie* result.

Nanopore Confinement of C-H-O Mixed-Volatile Fluids Relevant to Subsurface Energy Systems

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PROGRAM SCOPE

The overarching objective of this effort is to obtain a fundamental atomic- to macro-scale understanding of the sorptivity, structure and dynamics of simple and complex C-H-O fluids at mineral surfaces or within nanoporous matrices over temperatures, pressures and compositions encountered in near-surface and shallow crustal environments. To achieve this goal we (a) assess the adsorption-desorption behavior of methane, related hydrocarbons and CO₂ on a variety of mineral substrates and in nanoporous matrices, (b) characterize the microstructure and dynamical behavior of methane and related HC volatiles at mineral surfaces and within nanopores with and without H₂O present at relevant P-T-x subsurface conditions, and (c) utilize molecular-level modeling to provide critically important insights into the interfacial properties of these mineral-volatile systems, assist in the interpretation of experimental data and predict fluid behavior beyond the limits of current experimental capability. A scientifically diverse, multi-institutional team (Ohio State University, University College London, Oak Ridge National Lab, Pacific Northwest National Lab, Hunter College) are utilizing novel experimental and analytical techniques in concert with state-of-the-art theory, modeling and simulation approaches to address these issues. There is a special emphasis on building synergistic links between results obtained

from various neutron scattering and NMR studies which are integrated into our research portfolio with molecular dynamics modeling, to provide new phenomenological insights.

FY 2014 HIGHLIGHTS

Our research focuses on the behavior of simple and mixed volatile species such as CO₂, CH₄, C₂H₆, C₃H₈, H₂O and their mixtures confined to silica, alumina, titania and montmorillonite pores ranging in size from 1.5 to 35 nm. We use a combination of NMR and neutron scattering spectroscopy coupled with MD to probe the molecular behavior in the fluid-solid systems. Key results from these studies include: (1) Even for weak to moderate wetting fluids like the light alkanes and CO₂, respectively, the surface chemistry as well as pore size has a significant impact on changes in fluid density and volume of the adsorbed layer of a pure fluid as pressure and temperature increase. (2) The addition of a second carbon-bearing phase has a profound effect on the competition for sorption sites, phase chemistry and the dynamical properties of all phases present in the pore. (3) In addition to pores size, the extent of hydrophilicity (as -OH or H₂O) influences the selectivity of adsorption and associated hydrogen bonding of weakly interacting carbon-bearing species. (4) Low solubility phases such as methane may exhibit profound increases in concentration in nanopores in the presence of water at elevated pressures and ambient temperature compared to bulk values and even form clathrate cage structures.

A New Probe for Rock Elasticity - Time-of-flight Modulation (TOFM)

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

This project uses acoustic and vibrational spectroscopic measurements to isolate physical properties of porous rocks and finite-element modeling (FEM) to explore structure effects. The motive is the large reversible, (RNL) and irreversible, hysteretic, (HNL) nonlinear (NL) mechanical response of such materials and their fluid reservoir properties. The experimental program focused on fluids in a Berea sandstone sample. An extended experiment of removing and adding volatiles during measurements explored the mechanical-chemical interaction. Our experiments demonstrated that both RNL and HNL effects remain in the Berea sample when the vast majority of volatiles have been removed by heating and evacuation to UHV. Changing water content in clay components needs more study, but it seems the NL response is dominated by the silica structural network, which led us to study the link between the grain-bond-void scale and the macroscopic scales of the network. An FEM study was used to attempt to link the network and scaling of voids and bonds to the acoustic spectrum. Our model of grains and random bonds suggests that the identification of an elastic network with an equivalent homogeneous elastic solid is nontrivial, in that the modeled spectrum of vibrations of a random network are not reproduced by an homogeneous, isotropic, linear elastic solid with best-fit moduli, of the same boundary size and average density, up to the current size of the network model matrix (8x8x8). Clearly this requires more study since it is widely assumed that a sufficiently large number of randomly connected grains will behave as a homogeneous, isotropic solid.

FY 2014 HIGHLIGHTS

In the course of this project, two undergraduate students were trained, one continuing to a degree in geology at UNR and one moving to graduate work in geophysics at CalTech. The experiments and models produced large quantities of data, from which results were presented in talks and poster presentations at the AGU Fall Meetings in 2011-2013 and at two BES Geosciences meetings. The primary results are: that the fluid content influences, but is not responsible for nonlinear effects in Berea sandstone, and that the assertion that every porous network structure can be replaced with an equivalent linear homogeneous, isotropic elastic solid must be treated carefully since initial results suggest geometric nonlinearity and irreversibility of force-chain paths create deviations. Some related prior experimental results were analyzed and published as a book chapter [1] under the auspices of this project.

1. Nonlinear Elasticity and Hysteresis: Fluid-Solid Coupling in Porous Media, Alicia H. Kim (Editor), Robert A. Guyer (Editor) Wiley, On-line 2014, in print February 2015

Time-Lapse Seismic Monitoring and Performance Assessment of CO₂ Sequestration in Hydrocarbon Reservoirs

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Funding: \$213,520 (2014)

PROGRAM SCOPE

Our work focuses on fully integrating fluid flow and seismic data for monitoring injected CO₂ fronts by developing robust methods for reservoir characterization via coupled seismic and fluid flow modeling and joint inversion of seismic and fluid flow data. For computational efficiency and suitability for large-scale field applications, we are developing novel streamline-based compositional modeling of CO₂ sequestration including compressibility, stress-sensitivity, compositional and geochemical effects. We perform comprehensive simulations of the gas injection process accounting for the phase behavior of CO₂-reservoir fluids, the associated precipitation/dissolution reactions and the accompanying changes in porosity and permeability. The simulation results are then used to model the changes in seismic response with time. For data integration and uncertainty assessment, we adopt an efficient Bayesian framework using reversible jump multistage Markov Chain Monte Carlo (MCMC) methods.

FY 2014 HIGHLIGHTS

Our recent research efforts emphasized the development of reversible jump MCMC stochastic inversion algorithms for the automated upscaling (blocking) of acoustic well logs and for estimation of seismic impedance from seismic images. This approach has several practical advantages, one of the most important being automatic determination of the optimal parameter space during inversion. The routine application of the rjMCMC, however, can be computationally prohibitive for inversion of 4-D seismic data utilized for monitoring of fluid movements in the subsurface where data volumes are large. We have, therefore, investigated several approaches for accelerating computations. Some of the most

promising results apply novel multiscale finite element methods for simulating seismic wave propagation in heterogeneous reservoirs with changing fluid distributions. We have also continued our advancement of streamline based compositional modeling of CO₂ injection in hydrocarbon reservoirs. The novel aspect is the ability to incorporate gravity and capillary effects without adversely impacting computational efficiency. We use an orthogonal projection method to reformulate the streamline transport equations so that the fluxes of capillary and gravity are separated into components parallel and orthogonal to the total velocity defining the streamline trajectories. The orthogonal terms are calculated on the underlying three dimensional grid. The ability to effectively incorporate transverse fluxes in streamline transport calculations will be a step change in streamline simulation in general. We will demonstrate our proposed treatment of transverse fluxes using high resolution simulation of CO₂ migration in the subsurface with potential applications to both improved oil recovery as well as carbon sequestration.

Investigating the Physical Basis for Biomineralization

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Funding: \$460,000 (2014-2015)

PROGRAM SCOPE

This project is directed at determining principles that govern interactions of simple protein analogs and key inorganic impurities with carbonate minerals to direct the formation of hierarchical structures, polymorphs, and chemical signatures. The long-term goal is to establish the physical basis of biomineralization for applications to natural and engineered Earth systems.

FY 2014 HIGHLIGHTS

We made new insights into mechanisms of CaCO₃ nucleation in the pure system (Nielsen *et al.*, 2014, Science) and on organic templates (Hamm *et al.*, 2014, PNAS). The conventional assumption of the biomineral community is that an organic matrix templates nucleation by providing a stereochemical match that lowers the nucleation barrier during cooperative organization of ions. In contrast, materials disciplines view that simple binding assays can identify good promoters of nucleation. Our experimental study demonstrates low energy barriers correlate with strong crystal-substrate binding and reconciles the concept of stereochemical matching with the conventional wisdom that 'good binders are good nucleators'. The alternative perspectives become internally consistent through the lens of crystal-substrate binding. Using a novel *in situ* TEM approach, we also show that multiple pathways of nucleation occur simultaneously during homogeneous nucleation of CaCO₃, including direct and indirect formation of all crystalline polymorphs. Amorphous CaCO₃ (ACC) particles appear first, then are consumed by vaterite or aragonite that nucleate on ACC. Using isotopic labeling and mass spectroscopy, we also investigated factors that regulate ACC composition and the resulting crystalline products and Ca isotopic fractionation in ACC, calcite growth through an ion-by-ion process, and ACC that transformed to calcite while in contact with solution (Blue *et al.*, 2014; submitted; Giuffre *et al.*, submitted). Other pubs report direct observations of ACC nucleation, coalescence and crystallization via *in situ* TEM using an electrochemical fluid cell design developed with supplemental funding to this project. These are the first

measurements of their kind on natural mineral systems. We also applied this method to studying particle-mediated growth. The mechanism—as opposed to ion-by-ion attachment—is now recognized as a common phenomenon in diverse natural and synthetic systems.

Experimental Investigation of Flow-Induced Fabrics in Rocks at Upper-Mantle Pressures: Application to Understanding Mantle Dynamics and Seismic Anisotropy

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Funding: \$44,100 (2014)

PROGRAM SCOPE

Our project is an experimental approach to relevant Earth problems involving the flow of olivine-rich rocks in the upper mantle. We aim to quantify the rheological behavior of mantle rocks under simulated mantle conditions of high temperatures and high pressures. Measurements of stress, deformation rate, and deformation-induced crystallographic preferred orientation, which are components of the rheological relationship we seek to constrain, are carried out on samples inside the deformation-DIA using X-ray synchrotron radiation, and are conducted at beam line X17B2 at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. The goal of our research is to provide a better understanding of the flow strength and anisotropic features of both the lithospheric and asthenospheric mantle.

FY 2014 HIGHLIGHTS

We completed experimental runs on dry olivine during the past year and added to our database additional MTEX (Matlab)-derived information on *in situ* development of crystallographic preferred orientation (CPO) of grains during deformation, a valuable source of information related to seismic anisotropy in the upper mantle. Graduate student Nathaniel Dixon completed his thesis based on these data, and was awarded his Ph.D. degree in June, 2014. For dry, polycrystalline San Carlos olivine we find that at 1373 K and pressures from 1.5 to 9 GPa, the pressure dependence of flow in olivine is characterized by a value of the so-called activation energy of $14 \pm 3 \text{ cm}^3/\text{mol}$. This is a substantial effect, and given the >10 GPa pressure range of Earth's upper mantle, it is likely to have a pronounced effect on the thermal structure of the mantle, perhaps requiring temperatures to be warmer than otherwise expected. Shortly before the final shutdown and decommissioning of the NSLS synchrotron at Brookhaven, where we have carried out the bulk of our experimental runs over the past few years, we were able to do preliminary testing of a novel simple shear configuration in the deformation-DIA, which we hope to use in future runs at other synchrotron facilities (APS, NSLS-II). We are pleased to report that the new shear assembly performed nominally, and we should be able to employ it during our next beam time opportunity.

Collaborative Research: Evolution of Pore Structure and Permeability of Rocks Under Hydrothermal Conditions

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Funding: \$463,838 (2014)

PROGRAM SCOPE

Program scope: The transport properties of rocks can be altered by diagenetic, metamorphic, and tectonic processes. For example, porosity and transmissivity may be either increased or decreased by cataclasis, temperature or pressure cycling, pressure solution, plastic flow, crack healing, crack sealing or cementation. Similar processes are also critically important in industrial applications, including resource recovery, carbon-dioxide sequestration, and waste isolation. Often these mechanisms operate concurrently. In this project, we investigated the changes of permeability and pore geometry, owing to elastic deformation and inelastic straining of rocks by solution-transfer, pressure solution, and brittle fracturing, with and without metamorphic reactions. Better understanding of either the engineering or scientific applications requires the formulation of kinetics laws for each mechanism and the specification of the interactions among them. Thus, if loading conditions, mineralogy and kinetics laws were known, rates of porosity change for each process could be compared. But the relation between rate of porosity change and bulk properties must also be understood, because some processes are more efficient in changing permeability than others, e.g., neo-mineralization and microfracturing versus creep compaction. In this project, we used a combination of laboratory experiments, numerical calculations, and observations of microstructure to measure changes in pore volume, permeability, axial and volumetric strain rates under isostatic and conventional triaxial loading at elevated confining and pore pressures. The pore microstructure was observed using micro-CT, scanning electron microscopy, and laser confocal scanning optical microscopy. The data we obtained were used in network, finite difference and other numerical models to elucidate relations between permeability and other rock properties

FY 2014 HIGHLIGHTS

Pressure solution: We numerically simulated pressure solution creep of a three-dimensional, random pack of quartz spheres saturated with solvent fluid using a distinct element method, a non-linear contact model, and a model relating convergence rate at asperity contacts to local stress. Strain rates in the simulation were inconsistent with generic constitutive models characterized by constant activation energy and stress exponent. Instead, the data were better fit by two successive power laws proportional to t^ξ , where ξ was equal to 1 at very early times, but subsequently was as low as 0.3. The sensitivity of strain rate to stress in the simulations was significantly lower than 1 and varied with time. The apparent activation enthalpy was intermediate between that assumed for dissolution and diffusion, and decreased with time. Similar creep curves, including low values of the stress exponents, have been observed in unconsolidated packs of spherical NaNO_3 beads subjected to stresses low enough to prevent microcracking. Pressure dependence of transport properties and changes in pore connectivity and heterogeneity: In collaboration with workers from Southwest Petroleum University, Chengdu, we

performed permeability measurements on several tight sandstones to determine a non-linear, effective pressure law for permeability. We used network simulations to quantify the effect of pore connectivity and pore size heterogeneity on electrical formation factor during drainage of brine by a non-wetting and electrically non-conducting fluid (oil or gas) and to relate these changes to the geometrical and topological characteristics of the portion of the pore space saturated with brine. We also studied carbonate reservoir rocks with a bimodal distribution of large secondary, diagenetic pores contained within a porous, micro-granular matrix. Our current research studies the inter-relationship between permeability and the flow of an undersaturated fluid through carbonate rocks.

Impact of Micro- to Meso-Scale Fractures on Sealing Behavior of Argillaceous Caprocks on Carbon Sequestration

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Funding: \$107,000 (2014)

PROGRAM SCOPE

Wastewater and CO₂ injection may result in felt seismic events. We have pioneered a conceptual model/hypothesis that argues that a statistically significant number of the Mb 3.8–5.7 “induced” earthquakes are associated with injection into basal reservoirs or direct injection into crystalline basement rocks. Conductive basement faults are likely activated by injection due to the propagation of anomalous fluid pressures from the reservoir into the crystalline basement. Their occurrence in “tectonically quiet” regions indicates that in some cases we have an incomplete understanding of the dynamics and fate of fluids in the subsurface. In this proposal, we test our hypotheses that: 1. Injection into basal reservoirs promotes downward propagation of fluid pressure into crystalline basement rocks and increases the risk of induced seismicity, 2. Injection into overlying reservoirs with both top and bottom fine-grained seals will have a prophylactic effect. 3. We further hypothesize that conductive basement faults facilitate the propagation of elevated fluid pressures below sedimentary basins. We examine the geologic settings of injection site analogs, and characterize the structural and sedimentological features of the basal sedimentary rock–crystalline basement rock interface. We determine the rock properties at the bedrock–reservoir interface and evaluate the implications of these geomechanical characteristics for induced seismicity. We conduct field-based investigations of analog sites to assess the stratigraphic and structural controls on fluid pressure transmission at the bedrock–basal reservoir interface. Core samples collected from this basal reservoir will be used for laboratory geomechanical analysis. We will use data mining and statistical analysis for states with seismicity and those without to assess whether there is a statistical correlation between induced seismicity and basal reservoir injection.

FY 2014 HIGHLIGHTS

To date, we have:

- Conducted field work for basement-sediment interfaces to examine how small faults and fractures traverse the basement-sediment interface

- Defined cores from Michigan, Missouri, Kansas and Oklahoma that have the appropriate geological relationship, and we will visit these core this spring to study and sample
- Worked with an environmental nongovernmental organization to collate a wide range of data regarding injection rates and volumes for Class II injector wells in Ohio, West Virginia, Oklahoma, and Arkansas, and are mapping these injectors onto geologic basemaps
- We have mapped microseismicity in these states and are searching for spatial and temporal correlations between injection and seismicity

Physiochemical Evidence of Faulting Processes and Modeling of Fluid Flow in Evolving Fault Systems in Southern California

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 Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

Objectives: This is a collaborative study to quantify basinal fluid flow, submarine gas migration and diagenetic effects within deforming faults in a transpressional setting that is seismically active. The field application emphasis is on faulted basins in southern California. Project Description: We have mainly targeted active faults and young (Tertiary) petroleum fields in southern California for study. Faults include the Refugio Fault in the Transverse Ranges, the Ellwood Fault in the Santa Barbara Channel, and the Newport-Inglewood in the Los Angeles Basin. Subsurface core and tubing scale samples, outcrop samples, well logs, reservoir properties, pore pressures, fluid compositions, and published structural-seismic sections are being studied to characterize the tectonic/diagenetic history and geochemical signatures in carbonate that characterize rapid CO₂ degassing. These data provide constraints for finite element models that are being developed to predict fluid pressures, flow patterns, rates and patterns of deformation, subsurface temperatures and heat flow, and geochemistry associated with large fault systems.

FY 2014 HIGHLIGHTS

Measured gas flow data from a natural submarine seep area in the Santa Barbara Channel helps constrain fault permeability $k \sim 30$ millidarcys for the large-scale upward migration of methane-bearing formation fluids along one of the major fault zones. At another offshore site near Platform Holly, pressure-transducer time-series data from a 1.5 km deep exploration well in the South Ellwood Field demonstrate a strong ocean tidal component, due to vertical fault connectivity to the seafloor. Based on tidal-signal amplitude attenuation and phase shift at depth, we estimate permeability $k \sim 40$ millidarcys (hydraulic conductivity $K \sim 3 \times 10^{-8}$ m/s) and specific storage $S_s \sim 3 \times 10^{-6}$ m⁻¹. The tidal-derived hydraulic properties also suggest a low effective porosity for the fault zone, $n \sim 1$ to 3%. Our studies of faults in the Los Angeles basin, suggest an important role for the trapping of petroleum along the Newport-Inglewood fault zone (NIFZ). We constructed 2-D numerical models to characterize large-scale multiphase flow in this system. Our two-phase flow models replicated formation-scale patterns of petroleum accumulation associated with the basin margin, where deep faults resulted in stacked petroleum reservoirs, over time scales of ~ 300 kyr. The models also predict a strong preference for

focused upward flow along the NIFZ, confirming the structural controls. Furthermore, helium isotope data collected by my co-PI (J.R. Boles) document elevated leakage of fluids from the Earth's mantle along sections of the NIFZ near Long Beach, and our calculations indicated a fault permeability of about 2 to 20 microdarcys for ultra-deep fluid flow of 6 to 60 mm/yr.

Early Stages of Sea Urchin Biomineralization

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Funding: \$225,000 (2014)

PROGRAM SCOPE

Biominerals are crystalline, complex mineral systems formed by organisms. They master particle-by-particle rather than ion-by-ion crystal growth, thus they grow 100x faster and larger than synthetic crystals, with precise nano-, meso-, macro-morphology control, in environmentally-friendly conditions. Such skills, refined by 530 million years of evolution, could be harnessed for energy production, nanofabrication, or CO₂ sequestration. But first we must understand how natural biominerals form. Therefore, biomineral formation mechanisms, termed biomineralization, are of fundamental and applied interest. Here we study how sea urchin biominerals grow, and in particular the early stages of sea urchin biomineral formation mechanisms, collectively termed biomineralization.

FY 2014 HIGHLIGHTS

We identified that there is more than one mechanism at play in sea urchin biominerals as well as synthetic systems, forming by crystallization of amorphous precursor phases. Ion-by-ion and by particle-by-particle crystal growth take place concomitantly. This research was published in Gal *et al.* *Adv. Funct. Mater.* 24, 5420-5426, 2014.

Our subcontractors identified the role of Ca from seawater in the early stages biomineralization in sea urchin embryos. This work was published in Vidavsky *et al.* *Procs. Natl. Acad. Sci. USA* 111, 39-44, 2014.

Comparative Reactivity of Bacteriogenic and Abiogenic Mineral Nanoparticle Analogs

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Students: 1 Postdoctoral Fellow(s), 0 Graduate(s), 1 Undergraduate(s)
Funding: \$143,899 (2014)

PROGRAM SCOPE

The nanoscale forms of metal sulfides constitute a major fraction of the metal and/or sulfur loads in natural and anthropogenic systems. The origin, transport, and fate of nano-metal sulfides are relevant for a multitude of geological and environmental processes including biogeochemical cycling of elements,

environmental remediation, resource recovery, ecotoxicity evaluation, and biomineralization. Both biological and abiotic activities may contribute to the natural inventory of nano-metal sulfides. Yet, a basic understanding for the difference between the biogenic and abiogenic nanosulfides in terms of size, morphology, crystal structure, and surface reactivity is completely unavailable. And further, the mechanisms involved during the biological formation processes are poorly understood. This lack of information provides major motivation for our current project, which is composed of three major tasks. In Task 1, we compare the physicochemical properties (with an emphasis on size, crystallinity, crystal structure, and surface reactivity) of the metal sulfides (i.e., Zn-, and Fe-sulfides) produced via low-temperature aqueous pathways involving/not involving bacterial sulfate-reduction. Based on the results, we also aim to reveal the underlying formation mechanisms for the biogenic and abiogenic metal sulfides. As a follow-up (Task 2), we investigate the in-situ transformation/aging processes of the biogenic versus abiogenic nano-metal sulfides. And in Task 3, we examine and combine the findings of our experimental studies with field observations. The ultimate goal of the project is to obtain a systematic knowledge for the (trans)formation mechanisms of nano-metal sulfide and to illuminate the role of microbial activities in contributing to the inventory of nanoparticles in nature. The specific metal sulfides to be studied include Zn- and Fe-sulfides.

FY 2014 HIGHLIGHTS

In the past year, we have completed the major experimental work concerning the Zn-S system. Importantly, we have demonstrated that biological and abiotic processes at the same P-T conditions cause distinctive particle sizes, morphology, and crystal structure in the formed zinc sulfide nanoparticles. Briefly, the bacterial activities of dissimilatory sulfate reduction led to the formation of nanocrystals of mixed sphalerite and wurtzite phases resulting in high-density structural disorder (i.e., twins and stacking faults in the resulting nanocrystals). The primary size for the biogenic particles is in a range of ~3 - 12 nm. By contrast, the abiotic processes via titration/diffusion-controlled precipitation produced polycrystalline aggregates of ZnS. High-resolution images showed that these abiogenic aggregates are composed of randomly-oriented crystals with a primary size of ~1 - 2 nm. The aggregate size for the abiogenic ZnS is in a range of 15-30 nm. Further, we have revealed the underlying mechanisms involved during the biological and abiotic formation of ZnS nanoparticles. Overall, the formation of ZnS from aqueous solutions is a nucleation-dominated, crystallization-restricted process, manifested in the exclusive occurrence of ZnS nanoparticles in the biological and various abiotic systems. The difficulty in the ZnS crystallization likely stems from the surface instability of the ZnS growth units. This instability likely results from the permanent dipole moments on various important growth surfaces. In the biological system, the presence of polyanionic ligands may effectively screen dipolar surfaces by interacting with the polar faces of the growth units, and thus, the crystallization of the biogenic ZnS is significantly enhanced. We also found that the occurrence of structural dislocations (e.g., twins) in the biogenic ZnS is a direct consequence of the fore-mentioned crystallization pathway. All of this work is described in our latest manuscript.

Non-Darcian Flow, Imaging, and Coupled Constitutive Behavior of Heterogeneous Deforming Porous Media

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

Porous geomaterials exhibit a range of deformational responses under stress conditions typical of the earth's subsurface. Understanding these responses and quantifying the behavior mathematically is necessary to predict response of porous geomaterials for a variety of sub-surface geo-engineering pursuits for oil and gas production and exploration, as well as carbon sequestration in deep saline sandstone formations and depleted oil and gas reservoirs. Excluding time-dependent effects, porous rocks exhibit elasticity, have cohesion, are dilatant or compactant, fail with pressure dependence, and are frictional. These phenomena are collectively included in elastic-plastic constitutive modeling. This project consists of theoretical work aimed at improving constitutive descriptions of the elastic-plastic deformation of porous geomaterials in general and sandstone deformation in particular. The specific goal is to develop a thermodynamically rigorous constitutive framework that represents experimentally known behaviors of porous sandstone. In particular, the model seeks to capture two fundamental behaviors. First, the well-known experimental result that the plastic strain increment is not perpendicular to the yield surface. Second, the elastic moduli evolve with stress and with plastic strain. Commonly, the first is often modeled using non-associated flow with a plastic potential; however, this approach is not thermodynamically stable, since it admits the possibility of negative work. Capturing the second in a constitutive model is required to accurately predict plastic (permanent) deformation for a loading path of interest (e.g., field scale modeling of energy related activities).

FY 2014 HIGHLIGHTS

This work adapts the thermomechanics approach of Collins, Houlsby and colleagues (e.g., Collins and Houlsby, 1997), in which strains are determined from Gibbs free energy. Recent experiments on Castlegate sandstone reveal that the elastic moduli evolve with stress and plastic strain. The elastic strain consists of three components: 1) strain due to change in stress at a constant moduli, 2) strain due to stress dependence of the moduli, and 3) coupled strain due to plastic strain dependence of the moduli. The fourth component of total strain is the plastic strain, which is determined using a plasticity-like approach; however, the yield surface is represented in dissipative stress space, where the plastic strain increment is perpendicular to the yield surface. Subsequently, the yield surface in traditional stress space is found to be a translation and distortion of the yield surface in dissipative stress space; this distortion causes the plastic strain increment to be non-normal to the yield surface in traditional stress space. Preliminary expressions were developed for the evolution of the shear modulus (depends on shear stress and plastic shear strain) and the bulk modulus (depends on mean stress and plastic volume strain), using an existing Castlegate sandstone data set. These expressions were found to be not integrable. Therefore, we developed revised expressions for these moduli, which are integrable; the expressions include fitting constants which are being determined via curve fitting of the data set. The revised moduli expressions were integrated to obtain an expression for Gibbs free energy, with the caveat that a function of integration that depends only on plastic strain is yet to be determined. This function will be determined from the mapping function that maps the yield surface in traditional stress space to the yield surface in dissipative stress space, which will be completed in the next project year.

Fundamental Research on the Fractionation of Carbon Isotope During Photosynthesis: New Interpretations of Terrestrial Organic Carbon Within Geological Time

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Funding: \$122,000 (2014)

PROGRAM SCOPE

This research will quantify how pCO₂-dependent changes in plant carbon isotope fractionation affects the geochemical interpretation of the rock record. Our overarching goal is to produce a unified quantitative approach to the interpretation of carbon isotopes in the terrestrial organic record of the Phanerozoic specific to, and indicative of, the pCO₂ level of the time.

FY 2014 HIGHLIGHTS

We have performed multiple growth experiments involving both C₃ and C₄ plants that have quantified the relationship between pCO₂ and net carbon isotope fractionation across the levels of atmospheric pCO₂ hypothesized for the entire Phanerozoic using previous proxies. Our work has revealed an increase in net fractionation within increasing pCO₂ which is quite different for C₃ and C₄ plants, reflecting the different role of respiration between the two photosynthetic types. We have clearly demonstrated that the nature of carbon isotope fractionation in C₄ plants is quantitatively different from that seen in C₃, particularly over ambient-to-slightly-elevated levels (i.e., 400-1000 ppm). As of this writing we are in the middle of experiments designed to investigate levels up to 12,000 ppm, the level at which a hyperbolic model predicts near-asymptotic levels for C₄ plants. We have also suggested a new geochemical proxy for reconstructing paleo-pCO₂ based upon the carbon isotope value of C₃ plant content within terrestrial organic matter. Our recent work has focused upon demonstrating that this method accurately predicts pCO₂ level across a wide range of temporal resolutions and depositional environments via three independent tests. We tested the proxy's ability to reconstruct small (<100 ppm) changes in pCO₂ from carbon isotope measurements made on fossil leaves, bulk organic matter, and n-alkanes across the Last Glacial Maximum through the Holocene (30,000 to 100 years BP). We also tested the proxy's potential for improving models of atmospheric carbon release during carbon isotope excursions events by constraining estimates for the absolute minimum and maximum pCO₂ levels reached during these brief intervals of rapid pCO₂ rise and global warming.

EARLY CAREER: Nonequilibrium Physics and Phase-Field Modeling of Multiphase Flow in Porous Media

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Funding: \$150,000 (2014)

PROGRAM SCOPE

Carbon capture and geologic storage, dissociation of methane hydrates in permafrost, enhanced oil recovery, and water dropout in low-temperature fuel cells, all have something in common: two or more fluids flow simultaneously through a porous medium; and the displacement of one fluid by another is often unstable (either due to gravity or viscous forces). Yet, our ability to model multiphase flow mathematically at the macroscale has remained a challenge. The traditional equations are unable to predict, explain, or even reproduce, the formation of the complex patterns observed in experiments. The overarching goal of this proposal is to develop a new continuum theory of multiphase flow in porous media following a phase-field modeling approach, which recognizes that the system is out of thermodynamic equilibrium. The specific objectives are organized in three main thrusts: - Immiscible fluid displacements in a capillary tube and a Hele-Shaw cell. - Multiphase flow in porous media. - Application to CO₂ storage in saline aquifers. We propose a radical new approach---phase-field modeling---to advance our fundamental understanding and predictive capabilities of multiphase porous media flow. The basic tenet, with origins in the mathematical description of solidification processes, is that the system is far from equilibrium, and the energy of the system is a function of the inhomogeneous distribution of fluid phases in the pore space. This leads naturally to higher-order terms in the mass conservation equations. In recent work, we have used this formalism to develop a theory that explains and quantitatively predicts the formation of gravity fingers during infiltration into dry soil. The success of this application suggests that continuum models derived using the phase-field modeling framework have the potential to predict unstable multiphase flow in porous media.

FY 2014 HIGHLIGHTS

The project has led to the following publications and preprints during FY 2014:

- H. Gomez, L. Cueto-Felgueroso, and R. Juanes. Three-dimensional simulation of unstable gravity-driven infiltration of water into a porous medium. *Journal of Computational Physics*, 238, 217-239 (2013), doi:10.1016/j.jcp.2012.12.018.
- Zhao, C. W. MacMinn, M. L. Szulczewski, J. A. Neufeld, H. E. Huppert, and R. Juanes. Interface pinning of immiscible gravity-exchange flows in porous media. *Physical Review E*, 87, 023015 (2013), doi:10.1103/PhysRevE.87.023015.
- W. MacMinn and R. Juanes. Buoyant currents arrested by convective dissolution. *Geophysical Research Letters*, 40(10), 2017-2022 (2013), doi:10.1002/grl.50473.
- X. Fu, L. Cueto-Felgueroso, and R. Juanes. Pattern formation and coarsening dynamics in three-dimensional convective mixing in porous media. *Philosophical Transactions of the Royal Society A*, 371, 20120355 (2013), doi:10.1098/rsta.2012.0355.
- M. L. Szulczewski, M. A. Hesse, and R. Juanes. Carbon dioxide dissolution in structural and stratigraphic traps. *Journal of Fluid Mechanics*, 736, 287-315 (2013), doi:10.1017/jfm.2013.511.
- J. J. Hidalgo, C. W. MacMinn and R. Juanes. Dynamics of convective dissolution from a migrating current of carbon dioxide. *Advances in Water Resources*, 62, 511-519 (2013), doi:10.1016/j.advwatres.2013.06.013.
- B. Zhao, C. W. MacMinn, H. E. Huppert and R. Juanes. Capillary pinning and blunting of immiscible gravity currents in porous media. *Water Resources Research*, 50, doi:10.1002/2014WR015335 (2014).
- L. Cueto-Felgueroso and R. Juanes. A phase-field model of two-phase Hele-Shaw flow. *Journal of Fluid Mechanics*, 758, 522-552 (2014), doi:10.1017/jfm.2014.512.

- B. Zhao, C. W. MacMinn, and R. Juanes. Residual trapping, solubility trapping and capillary pinning complement each other to limit CO₂ migration in deep saline aquifers. *Energy Procedia*, 63, 3833-3839 (2014).
- M. Strait, M. Shearer, R. Levy, L. Cueto-Felgueroso and R. Juanes. Two fluid flow in a capillary tube. *Springer Proceedings in Mathematics & Statistics*, 109, 149-161 (2015), doi:10.1007/978-3-319-11125-4_14.

EARLY CAREER: In-Situ Thermodynamics Measurements at Metal Oxides-Solution Interfaces Using Flow Adsorption Microcalorimetry

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 Funding: \$750,000 (2014-2019)

PROGRAM SCOPE

Chemical reactions at interfaces between metal oxides and aqueous solutions play a fundamental role in environmental, geological, planetary and technological settings. Our ability to harness metal oxides (MO) potential in technological applications and safeguard the future of our environmental resources under realistic operating and environmental conditions hinges on our ability to adequately model interfacial chemical reactions – protonation, deprotonation, ion exchange, adsorption, desorption, etc. A host of theoretical principles, experimental techniques and computational methods have been utilized to the study of the complex spectrum of interfacial reactions. Yet conspicuously missing are thermodynamics data, specifically those coming from direct measurements. The overarching goal of this project is to complete a systematic study of the thermodynamics properties of interfacial reactions at four MO surfaces (Rutile (α -TiO₂), Quartz (SiO₂), boehmite (γ -AlOOH) and goethite (α -FeOOH)) through the application and construction of novel flow adsorption microcalorimetry techniques and instrumentations. These unique and specialized microcalorimeters will operate at various temperatures and solution chemical compositions allowing for in-situ measurements across metal oxides and ligands of various characteristics. The overall research goal will be accomplished by completing the following three specific objectives (O): O₁) Determine the energetics of surface protonation and deprotonation, ion exchange and ligand sorption reactions; O₂) Investigate the surface charge thermodynamic properties under a range of temperature and solution chemical compositions; and O₃) Develop predictive trends of the interplay between MO structure, surface coverage and surface reactivity. In addition to key thermodynamics parameters, calorimetric measurements provide a wealth of mechanistic information about reactions energetics and kinetics, surface charge characteristics, and structure-reactivity relationships.

FY 2014 HIGHLIGHTS

The project start date was July 15, 2014. The major accomplishments of the project within the 2.5 months of fiscal year 2014 were:

- 1) expanding the calorimetry operations to a newly upgraded and larger laboratory space to accommodate the building of the proposed instrumentations,
- 2) hiring a postdoctoral fellow and one master student. Both started on August 4th,

- 3) completing the redesign of the microcalorimeter electronic board, and
- 4) concluding the construction of the first upgraded flow adsorption microcalorimeter which was dedicated to collecting data on rutile.

Adsorption Equilibrium and Kinetics at Goethite-Water Related Interfaces

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 Funding: \$90,141 (2014)

PROGRAM SCOPE

The comprehensive project, GEOCHEMISTRY OF INTERFACES: FROM SURFACES TO INTERLAYERS TO CLUSTERS, to which this research is a component seeks to identify and evaluate the critical molecular phenomena at the metal-oxide interface that control many geochemical and environmental processes. Specific tasks include the analysis of surface speciation, adsorption phenomena, surface complexation modeling, ion pairing, interlayer structures, parameterization of edge surfaces of clay minerals, and synthesis of molecular clusters as well as the structure and reactivity of their surfaces sites. Theoretical efforts emphasize the use of large-scale molecular dynamics simulations, *ab initio* molecular dynamics, and related density functional theory and classical methods to address structure and thermodynamics of mineral-water systems. Spectroscopic evidence is provided by X-ray absorption, second harmonic generation, sum frequency generation, infrared and Raman vibrational spectroscopies. Macroscopic data in traditional batch and column experiments is used in conjunction with molecular techniques to develop predictive models that characterize sorption in complex systems containing a wide range of background solution compositions. Our studies have focused on systems involving alkaline earth metal (Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+}) and heavy metal (Hg^{2+} , Co^{2+} , Cd^{2+} , Cu^{2+} , Zn^{2+} , Pb^{2+}) cations. The anions we have selected for study include Cl^- , NO_3^- , ClO_4^- , SO_4^{2-} , and CO_3^{2-} , SeO_3^{2-} because these represent a range of potentials for forming ion-pairs or ternary complexes with the metal ions studied. Ion adsorption and the potential formation of ion pairs and ternary complexes on clays and clay minerals such as silica (quartz, amorphous silica), alumina (corundum and gibbsite), and ferric iron (goethite) oxides have been examined as part of this project and the overall comprehensive project.

FY 2014 HIGHLIGHTS

Research in FY 2014 focused on collection and analysis of adsorption data for the alkaline earth metal ions. Macroscopic adsorption studies were conducted over a range of ionic strengths, pH values, and cation-to-sorbent concentration ratios in order to elucidate the surface complexation reactions of these cations. One significant trend that was found from our test results was that the impact of ionic strength on metal cation adsorption on goethite increases proportionally with the crystal radii of the cations, which follows: $Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$. This trend differs from that observed in our previous molecular modeling and macroscopic data work with gibbsite. The cause of these different trends is likely due to the relative adsorption affinity relative to the pH_{pzc} of the aluminum and iron oxide. Preliminary surface complexation modeling indicated that Mg sorption could be described over a range of ionic strengths using the same CD-MUSIC electrolyte and surface ionization parameters used for our Pb, Cd and selenite modeling on goethite. Mg^{2+} and Ca^{2+} adsorption on goethite were also tested at reduced temperature

(4°C) in order to examine the relationship between hydration energies and adsorption behaviors of the cations. In general, reduced temperatures should reduce the removal of waters from the hydration shell of cations, and hence lead to less adsorption and more outer-sphere complexes. In this study, the lower temperature slightly reduced the adsorption of Mg^{2+} , whereas Ca^{2+} was not affected. The reduced adsorption of Mg^{2+} is consistent with molecular modeling results and previous macroscopic data in which adsorption of metal ions was enhanced by elevated thermal energy and there was a concomitant shift from outer sphere to inner sphere with increasing temperature.

Interfaces Under Extreme Conditions: Stable Isotope Behavior of Redox Reaction and Hydrothermal Reactivity of Transition Metals.

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Funding: \$137,999 (2014)

PROGRAM SCOPE

The goal of this research program is to develop and test predictive theories for isotope fractionation during electrochemical reactions. Measurements in a wide variety of metal deposition systems including Fe, Zn, Li, Mo, and Cu have led to observations of large, tunable isotope fractionations as a function of rate and temperature. In our previous studies, we have separated the influences of mass transport and electrode behavior on the overall observed isotope signature. Our next set of studies will be designed so that mass-transport processes are not the rate-limiting reaction step in order to study the isotope signature of electron transfer reactions. We will undertake a combination of computational studies, experiments, and analytical work that will predict, generate, and measure stable isotope fractionation during electrochemical reactions. We will investigate the electrochemical isotope effect of the following systems that are interesting in the environmental and geological sciences. We will measure isotope fractionations associated with the reactions between ferric (Fe^{+3}) and ferrous (Fe^{+2}) iron in a variety of aqueous environments, including salt water. We will examine isotope fractionation during electro-reduction of mercury to examine the multi-stable isotope behavior of heavy elements during chemical reactions. Finally, we will examine the temperature-dependent electroreduction of lithium, in order to investigate processes to optimize separation of lithium isotopes.

FY 2014 HIGHLIGHTS

Abstract: Stable isotopes are sensitive indicators of physical and chemical processes at solid/liquid interfaces away from equilibrium. The goal of this research program is to study how and why stable isotopes of metals fractionate during electrochemical reactions. Summary of Progress: Measurements in a wide variety of metal deposition systems including Fe, Zn, Li, Mo, and Cu, have led to observations of large isotope fractionations that strongly vary as a function of rate and temperature. We interpret our observations in terms of a competition between two rate-limiting steps: mass transport to the interface, which results in small isotope signatures, and the electrochemistry step, which results in much larger isotope signatures. Our results are consistent with a theory predicting isotope-dependent electrochemical reaction rates that is based on Marcus electrochemical theory, and imply that isotope behavior at a heterogeneous interface is sensitive to the kinetic behavior of the interface. Based on ours

and others' observations and existing chemical kinetics theories we are developing theories of isotope-dependent interface reactivity that can explain our observations and predict isotope fractionations in a wide variety of interfacial chemical processes.

2014 published papers, manuscripts, and conference abstracts and presentations:

J. R. Black, S. G. John, A. Kavner, (2014), Coupled effects of temperature and mass transport on the isotope fractionation of zinc during electroplating, *Geochim. Cosmochim. Acta*, 124, pp. 272-282.

A. Kavner, J. R. Black, and W. F. McDonough, Temperature dependence of lithium isotope separation during electroplating: Predictions and measurements. (manuscript in progress)

Invited review paper: "Isotope Electrochemistry" for *Electroanalytical Chemistry*, A. Bard and C. Zoski, eds. (manuscript in progress)

Invited Keynote Speaker, Gordon Conference on Electrochemistry, Jan 2014, Isotope Electrochemistry, A. Kavner.

Computational and Experimental Investigations of the Molecular Scale Structure and Dynamic of Geologically Important Fluids and Mineral-Fluid Interfaces

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Principal Investigator: R. James Kirkpatrick

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Funding: \$184,459 (2014)

PROGRAM SCOPE

Research supported by this grant and the closely linked DE-FG02-10ER16128 (G. M. Bowers, PI, Alfred University) focuses on addressing fundamental scientific questions regarding the structure, dynamics, and reactivity of geochemically important fluids, fluid-mineral interfaces, and confined fluids on a molecular scale using a combination of computational molecular modeling and spectroscopic methods, primarily nuclear magnetic resonance (NMR) spectroscopy. The Michigan State group is responsible for the computational modeling and part of the NMR experiments. The Alfred group is responsible for the wet chemistry and most sample synthesis, much of the basic sample characterization, and much of the NMR spectroscopy. Collaboration between the two groups is very close, with computational modeling motivating the spectroscopic studies and the spectroscopic results helping to identify key questions for computational modeling. The combination of computational and spectroscopic approaches is highly effective in addressing otherwise intractable molecular scale problems concerning the physical and chemical behavior of fluids and interfaces, which are central to understanding such geological problems as the migration of chemicals in soils, sediments, and rocks, and the processes by which fluids alter these host materials. The objectives during this grant period include developing a deeper understanding of molecular-scale structure and dynamics in clay-natural organic matter (NOM) composite materials that are ubiquitous in soils, sediments, and many sedimentary rock types. We are providing key new insights into how NOM, a key sink for many inorganic and organic contaminants, influences the binding and dynamics of cations, aqueous fluids, and supercritical CO₂ in the composites; the binding structures and mechanisms of NOM-mineral association under a variety of geochemical conditions; and how NOM influences the physics of composite hydration.

FY 2014 HIGHLIGHTS

During 2014, research supported by this grant focused on fundamental understanding of the structural environments and dynamics of water and cations in swelling clays, how chemical conditions control the structures and molecular-scale ion and fluid behaviors in composites composed of the smectite mineral hectorite and Suwannee River natural organic matter (NOM), and the molecular scale interactions of mineral surfaces, aqueous fluids, and CO₂ at pressure and temperature conditions relevant to geological C-sequestration reservoirs. Variable temperature ²H NMR of smectite containing different exchangeable interlayer cations shows that the hydration energy of the cation controls the rate of exchange of water molecules between different types of structural environments in the interlayer galleries. Computational molecular modeling of the rate of water exchange between the cation hydration shell and bulk solution explain these results well. Helium-ion microscopy (HeIM) and X-ray diffraction (XRD) show that the nano-scale structure of clay-NOM composites depend sensitively on the chemical properties of the cation, pH and the ionic strength of the aqueous solution in which they form. Composites with both homogeneous and heterogeneous nano-scale structures form. ¹³C, ²³Na, ⁴³Ca, and ¹³³Cs NMR data provide direct evidence of the close interaction of CO₂ with clay-NOM composites and show that the chemical properties of the cations significantly influence CO₂ dynamics. Computational modeling is beginning to provide a molecular scale understanding of these results. Model results show that with Na as the exchangeable cation, NOM molecules are not tightly held to the mineral surface when only water is present, whereas with only CO₂ present they are. With both water and CO₂ present, the NOM molecules migrate away from the water-saturated mineral surface and accumulate and aggregate at the H₂O-CO₂ interface.

Experimental Investigation of Flow-Induced Fabrics in Rocks at Upper-Mantle Pressures: Application to Understanding Mantle Dynamics and Seismic Anisotropy

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Funding: \$147,747 (2014)

PROGRAM SCOPE

The focus of this study is to quantify the rheological behavior and deformed-induced fabric of mantle rocks under simulated mantle conditions including experiments at high temperatures and high pressures. The goal of our research is to provide a better understanding of the rheological behavior and its anisotropic features of both the lithospheric and asthenospheric mantle.

FY 2014 HIGHLIGHTS

Quantification of low-T plasticity of garnet: The low-temperature plasticity of polycrystalline garnet has been experimentally investigated at high pressures (~4 to 9 GPa) and relatively low temperatures (773 ≤ T ≤ 1273 K) under anhydrous conditions. Experiments were carried out using a deformation-DIA apparatus on the beamline at Brookhaven National Laboratory. In a run, differential stress and sample displacement were monitored in-situ using synchrotron x-ray diffraction and radiography, respectively. The low-temperature plasticity of garnet is constrained by our data with a value for the Peierls stress of

9.8 ± 0.3 GPa, a critical constraint on the rheological properties of subducted lithosphere. Creep behavior of enstatite at high pressures: The deformation behavior of fine-grained enstatite was investigated at high pressures (4.2 to 6.9 GPa) and high temperatures (1373 to 1573 K). Based on results from this study, the creep behavior of enstatite under anhydrous conditions has been quantitatively presented in the form of a flow law that describes the dependence of deformation rate on stress, temperature, and pressure. Specifically, a non-linear, least-squares fit of our data yields the dependence of creep rate on stress with an exponent of $n \approx 1$, indicating that samples were deformed in the diffusion creep regime. Experimental results also yield the dependences of creep rate on temperature and pressure with an activation energy of ~ 250 kJ/mol and an activation volume of $\sim 3.5 \times 10^{-6}$ m³/mol, respectively. The flow laws for enstatite, one important constituent component for the upper mantle, quantified from this study provides a necessary database for modeling the dynamic activities occurring deep within Earth's interior.

Transport and Clogging of Particulate Flow in in Fracture Systems

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Funding: \$130,919 (2014)

PROGRAM SCOPE

Fluids recovery from subsurface reservoirs is complicated by the presence of suspended solid particles which can reduce throughput and contaminate the efflux, and may even accumulate locally to form a jammed or clogged structure which blocks the flow. Transport via connected fracture networks provides the most effective means of fluids recovery in practice, but fracture flow is typically dominated by channeling into a limited number of flow paths and is particularly sensitive to clogging. A detailed understanding of the conditions under which jams form, their response to controlled perturbations in the flow, and their global effects on transport will enhance our understanding of the dynamics and improve our ability to extract subsurface fluids. In previous work we have used numerical simulations based on the lattice-Boltzmann method to study the transport of non-colloidal suspensions in open fracture joints, with realistic self-affine surface roughness. More recently, we considered the contrasting case of a tight fracture, where the mean aperture is so small that sub-regions of width comparable to or smaller than the particle size are present. In this case particles are prone to jam - fixed single particles or clusters of immobilized particles appear and partially block the fracture. We studied the stress distribution and investigated flow protocols which can release jammed particles.

FY 2014 HIGHLIGHTS

A key aspect of flow in fracture systems is the behavior at the junctions where individual fracture joints intersect. We have begun with the simplest case of two self-affinely rough fractures meeting at a right angle, each containing a packet of suspended particles which collide near the intersection. The motion of a particulate suspension in this geometry is calculated by lattice-Boltzmann methods, which allow us to monitor flow and stress fields as a function of time and at fine resolution, below the particle size. The system is periodic in all three directions, so that the particle packets repeatedly pass through the fractures after crossing the boundary and recollide at the junctions, simulating the effect of multiple

junctions in a fracture network. We observe gradual fragmentation of the packets of particles, in general in an asymmetric manner despite the geometrical symmetry of the system, although the detailed mixing behavior varies in different realizations. One striking observation is that, as with the single-fracture jamming case studied previously, varying either the initial particle positions or the fracture surfaces can qualitatively alter the behavior. A second notable feature is that the extra space provided by the junction and the collisional interaction combine to broaden and dilute a particle packet, a point very relevant for unblocking particle jams.

Internal Erosion, Particle Transport, and Channelization Drive by Fluid Flow

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Funding: \$63,260 (2014)

PROGRAM SCOPE

The goal of the project is to investigate internal erosion and transport of particles in sediment beds leading to heterogeneity and channelization of the sediment bed driven by fluid flow. Understanding this system is of fundamental importance to a number of geophysical processes, and in the extraction and sequestration of hydrocarbons in the subsurface. The project builds on a three-phase model to describe development of channel networks in a bed composed of particles through erosive instabilities. A fluid flowing through a solid disordered medium is considered to slowly convert a small amount of solid phase to a mobile phase because of hydrodynamic phases. This mobile phase is then advected by the fluid phase and can also get deposited further downstream. The resulting changes in porosity can then lead to a feedback loop resulting in instabilities and development of inhomogeneities in the spatial field. In order to calibrate and refine the model, experiments are developed to observe the evolution of the erosive features as a function of driving parameters and the bed composition. Of particular importance to obtain physically relevant results is accurate local erosion laws and rheology of the fluid phase due to the presence of the eroded material. We perform complementary experiments with simplified erodible porous interfaces under prescribed normal and tangential fluid flow conditions corresponding to the bed compositions in the first series of experiments. These investigations will provide the erosion and deposition rates under well-defined normal and shear stress conditions. This multi-faceted approach will enable us to obtain an integrated picture of internal erosion of an erodible medium starting from the pore scale to the scale approaching that of a reservoir.

FY 2014 HIGHLIGHTS

We performed a systematic investigation of the erosion threshold of sedimented beds driven by a fluid flow as a function of grain size and grain roughness. Experiments were performed with a bed in a model enclosed cylindrical channel under laminar flow conditions. The shear rate at threshold for a prescribed flow rate is obtained from the height of the fluid above the bed as it comes to rest, and used along with the grain size to determine the particle Reynolds number. We calculated the critical Shields number given by the ratio of the viscous shear stress and the normal gravitation and buoyancy stresses at the threshold of motion. We found that bed armoring leads to a systematic significant increase in the critical Shields number independent of the grain roughness. This observed increase is of the same order of

magnitude as scatter reported in the literature when the critical Shields number is drawn from different data sets. While comparing similarly prepared beds with increasing particle size, we found that the critical Shields number decreases systematically with the particle Reynolds number, in contrast with the Shields curve which is constant at low particle Reynolds number. We found that particles rotate out of the pockets in the bed rather than sliding out. Accordingly, we used the condition of torque balance at threshold to determine the critical torque needed to dislodge grains due to viscous drag. This torque is found to be significantly lower than the value needed to dislodge a spherical grain on the bed surface which is fully exposed to a linear shear flow. Thus, we are able to obtain the degree of exposure that particles experience at threshold for freshly prepared as well as for armored beds. These experiments provide a complete picture of the threshold for erosion which we can now use to obtain sediment flux rates as a function of Shields number.

Reaction-Infiltration Instabilities in Fractured and Porous Rocks

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Sr. Investigator(s):
Students: 1 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding: \$156,135 (2014)

PROGRAM SCOPE

We are using numerical and analytical methods to investigate the dissolution of fractures and porous media. The knowledge obtained from these investigations will be used to construct models for the change in fracture permeability in dissolving rocks. Our goal is a model that incorporates the key feature of dissolution -- namely its strong spatial inhomogeneity -- in a sufficiently simple way that it can be used to improve the accuracy of permeability models at the reservoir scale.

FY 2014 HIGHLIGHTS

The final paper in our extensive study of the stability of dissolution fronts in fractures and porous media was published in the Journal of Fluid Mechanics [Reactive infiltration instabilities in rocks. Part 2. Dissolution of a porous matrix J. Fluid Mech.,738, 591-630, 2014]. There are two further manuscripts in preparation (i) Mechanisms for volume preserving replacement under review for Geophysical Review Letters (ii) Dependence of dissolution patterns on the initial aperture distribution in rough fractures - in preparation for Journal of Geophysical Research. We have completed a Darcy-scale solver for reactive transport in two and three dimensions. It is coupled to the LLNL HyPre library for a rapid parallel solution of the linear equations. The code can has been used to track the dissolution of two and three dimensional systems containing up to 10^8 elements. We are developing fully three-dimensional solver for fracture dissolution, based on the OpenFOAM toolkit. We have made a number of extensions to the OpenFOAM library to model the motion of dissolving surfaces in 3D. The code currently solves fracture dissolution problems in parallel, using linear reaction kinetics. Extensions to more realistic chemistry are in progress.

Predicting Fracture Porosity Evolution in Sandstone

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Sr. Investigator(s): Jon Olson; Texas-Austin, University of
Robert Lander; Texas-Austin, University of
Linda Bonnell; Texas-Austin, University of
Peter Eichhubl; Texas-Austin, University of
Students: 1 Postdoctoral Fellow(s), 4 Graduate(s), 1 Undergraduate(s)
Funding: \$288,000 (2014)

PROGRAM SCOPE

Evidence of how fracture growth and diagenesis interact to create and destroy fracture porosity is preserved in quartz cement deposits in otherwise open fractures. Using textures and fluid inclusion data combined with burial histories allows inference of duration and rates at which fractures open, testing of a structural diagenetic model that accounts for how fracture porosity and rock properties change as a function of thermal exposure. Results include accurate prediction fluid flow characteristics of fractured rocks based on coupled effects of diagenesis and deformation. Experiments measure how rock and fracture properties evolve with diagenesis. Current research is documenting and modeling the opening histories of entire fractures and fracture arrays in contrasting tectonic and thermal regimes and developing and testing a fully coupled diagenetic-geomechanical model.

FY 2014 HIGHLIGHTS

The capacity of a structural diagenetic approach to unravel previously indistinguishable fracture causes was demonstrated in several integrated studies. A Colorado example shows fractures formed in response to gas generation in adjacent shales and coals under high pore fluid pressure; a Mexico example shows fractures opened primarily under tectonic extension. Two studies using outcrop and core data, kinematic and dynamic structural models and fracture growth reconstructions show complex fracture growth. A two-stage non-linear growth history was demonstrated in a Texas example using textural reconstruction and fluid inclusion microthermometry. We described how rock type and diagenesis governs near-fault fracture size, openness and fault strength. We published our model that accounts for crystal growth patterns and internal textures in quartz cement in fractures, including massive sealing deposits and veneers on open fracture surfaces and bridge structures that span otherwise open fractures. A new code predicts extent of fracture bridging by quartz cement, accounting for euhedral/non euhedral nucleation surfaces, crystal size, temperature, and fracture opening and allows efficient accounting for these effects in our geomechanical model. A new technique to quantify fracture spacing applied to fracture arrays where we are testing a model that predicts size scaling based on fracture cohesion explores how fracture spatial arrangement and cementation may be related. Diagenetic modeling and laboratory experiments show how fractures, cement textures, and mechanical properties evolve with progressive diagenesis. Experimental fracture diagenesis in the laboratory created artificial cement using a wide range of pore fluids and host minerals to test elements of fracture growth and diagenesis models. In the context of project findings we published reviews of fracture size-scaling in sandstone, microfractures and fractures in shale. Papers: www.jsg.utexas.edu/sdi/

Porous Rock with Fluid: Heterogeneity, Scale of Measurement and Transforms

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Funding: \$450,000 (2014-2016)

PROGRAM SCOPE

Rock properties, such as porosity, permeability, electrical conductivity, and the elastic moduli vary in space and, hence, lack spatial stationarity within a selected rock volume. As a result, such data depend on the scale and position of measurement. This natural variability renders ambiguous the concept of a data point, simply because the datum will be different just a few inches away, or if assigned to encompass a larger volume. Yet, there is no alternative to using the results of controlled experiments conducted at one scale for interpreting data acquired at a very different scale. Therefore, our main question is: How to apply a rock physics operation throughout a range of scales. Based on previous results, we assume that transforms between a pair of rock properties exhibit much less scale sensitivity than the properties themselves. To test this hypothesis, one needs to conduct the same experiment on different portions of a rock volume by changing both the size and location of the test. This is problematic in the physical lab. Hence, the main experimental tool we selected is computational rock physics. The common thread of the proposed effort is utilization of digital experiments in exploring the scale dependence of relations between rock's porosity and permeability; porosity and electrical conductivity; porosity and elastic moduli; as well as cross-property relations among the said rock properties. This approach will guide us in using rock physics laws obtained in the digital and/or physical laboratory (at a scale of mm and cm) at the field scale of feet and meters. The basic-science deliverable will be a quantitative insight into the impact of the scale of a process on relations between rock properties that govern this process. The practical deliverable will be a basis for using the digital and physical laboratory data at a practical field scale.

FY 2014 HIGHLIGHTS

The highlights of FY 2014 are: (a) macroscopic permeability-porosity behavior in composites constructed from elements with given permeability-porosity transforms; (b) effects of fabric heterogeneity in cemented particulate medium – computational study using the discrete element method; and (c) stress heterogeneity in pore space – computational study using the finite-element method. In the first investigation, the percolation through porous media was analyzed by using a Darcy flow simulator in a random composite with properties taken from two data sets: Ottawa sand with kaolinite and Fontainebleau sandstone. Percolation has two distinctive regimes: one stable, for composites with a large number of elements where adding more elements has weak effect on percolation; and the other, for smaller composites, where both the number of the elements and the amount of low- and high-permeability elements control percolation. In the second investigation, we conducted numerical simulations on granular media targeting the effects of cementation on stress heterogeneity in pre-compacted granular media. We show the existence of stress heterogeneity even if the strain is homogeneous. Cementation mechanism where cement is deposited evenly on grain surfaces acts to increase this heterogeneity for low cement volume and to reduce it for higher cement volume. Where cement is only deposited at the grain contacts, the impact on effective elastic heterogeneity depends on

the heterogeneity of cement distribution among the contacts. In the third investigation, we explored how stress heterogeneity affects fluid and solid substitution in porous rock. We numerically estimated and compared the stress variation inside idealized ellipsoidal inclusions and realistic pore space. We observed significant stress variation in the pore space of Fontainebleau digital samples, which appears to have an effect on parameters used in theoretical fluid and solid substitution.

Multiscale Modeling of Multiphase Flow, Transport, and Reactions in Porous Medium Systems

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Funding: \$187,043 (2014)

PROGRAM SCOPE

Our work is directed at constructing models of multiphase porous medium systems that are consistent across length scales. Because it is the only method employed ensuring that thermodynamic relations as well as conservation equations can be related to smaller scale precursors, we are advancing the thermodynamically constrained averaging theory (TCAT) in this work. TCAT has the features that (i) all macroscale variables are defined explicitly in terms of microscale properties; (ii) closure relations are advanced that are consistent with the second law of thermodynamics; (iii) models can be constructed at a range of length scales, up to the system scale; (iv) hierarchical families of models can be developed with varying degrees of sophistication consistent with physical system of interest; and (v) interscale consistency facilitates the use of simulations and experimental studies performed at one scale to support the findings at a different scale. The specific objectives of this project include formulating, closing, and applying three types of models: (1) a two-fluid-phase flow model, (2) a two-fluid-phase flow and species transport model, and (3) a three-fluid-phase flow model. This work involves a theoretical component to formulate candidate models, a pore-scale modeling component to guide the formulation of specific closure relations, and a continuum-scale numerical methods component to approximate the formulated macroscale models.

FY 2014 HIGHLIGHTS

Highlights for this year's accomplishments include: (1) publication of a book detailing the development of the thermodynamically constrained averaging approach; (2) completion of a book chapter that validates aspects of the theory for two fluid phase flow using high resolution lattice Boltzmann computations and microfluidic experiments; (3) advancement of computational methods for performing large-scale simulations at the pore scale that provides a means to directly connect the microscale quantities with macroscale quantities that appear in the theory; and (4) extension of the theory to the case of two fluid phase flow and species transport.

Thermodynamics of Minerals Stable Near the Earth's Surface

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Funding: \$241,888 (2014)

PROGRAM SCOPE

This project uses specialized calorimetric techniques in the Peter A. Rock Thermochemistry Laboratory at UC Davis to obtain new thermochemical data for materials, often of nanoscale dimensions, encountered in the Earth's "critical zone," the near surface region of the planet most directly affecting and affected by human activity. This project focuses on the transformations from ions in solution to clusters, to nanoparticles, to precipitates, and finally to well crystallized minerals (and the reverse transformations during weathering and dissolution) representing a continuous spectrum of events. This project expands on our previous studies of the energetic driving forces for such transformations, with a strong emphasis on transition metals and redox reactions, especially involving iron and manganese oxides. We continue exploring the gradual transformation from nanoclusters in solution to nanoparticles to crystalline minerals, with an emphasis on transition metal oxides of variable valence, especially iron and manganese. A new area is the large effect of particle size on the thermodynamics of redox reactions. To succeed in calorimetry on the above problem, we must fine tune calorimetric, analytical, and structural techniques to control and delineate oxidation states, water contents, and structural features of materials containing one or more transition elements of variable valence and structural and adsorbed H₂O. In particular, we are confident now that we can do reliable oxide melt solution calorimetry on phases which simultaneously contain ferrous and ferric iron and water, as well as materials containing several transition metals. This capability opens the door to detailed studies of minerals containing these combinations of elements, for which enthalpies of formation are still surprisingly poorly known. These include spinels containing Cr, Mn, Fe, Co, Ni, and Cu, as well as complex sulfides, silicates, and borates containing transition metals.

FY 2014 HIGHLIGHTS

Nancy Birkner completed her Ph.D. thesis on manganese oxides and is now a postdoc with Prof. Peggy O'Day at UC Merced. The final part of her thesis concerned layered and tunnel structured phases. These manganese oxides (birnessite, etc.) contain Ca, Na, and/or K, as well as water. They are typically nanophase and charge balance is achieved by interlayer or tunnel cations and by vacancies. Our earlier studies determined the energetics of formation of several of these phases using synthetic sample but did not consider the effects of particle size and surface energy. We returned to these materials with the hypothesis that they, like the CaMnO catalyst phases which have higher Ca content than natural materials, have low surface energies which help stabilize them as fine grained materials. By controlling the ionic strength of the electrolyte during synthesis, Birkner synthesized several series of materials with virtually identical cation contents and average manganese oxidation states but different particle sizes. The surface energies of the layered and tunnel structure complex manganese oxides are confirmed to be significantly lower than those of the binary manganese oxide phases. The surface energy of the complex manganese oxides appears to decrease with decreasing manganese average oxidation state, with greater mixed manganese valence. We are exploring whether the measured thermodynamic properties allow us to understand the sequence of formation and transformation of these phases in natural and industrial settings. Lili Wu completed her Ph.D. thesis on the energetics of zeolite formation by studying heats of formation of aluminosilicate zeolites containing transition metals. The energetic trends are similar to those for other ternary transition metal oxide materials, e.g spinels. Dana Reusser is

completing her thesis on the energetics of aluminum Keggin clusters in the solid state and in solution. New data are being analyzed and prepared for publication.

The Physics of Swarms in Fractures: Functionalization Particles and Programmable Seismic Scatters

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Funding: \$121,264 (2014)

PROGRAM SCOPE

The objective of this research is to determine how to control the injection and retrieval of sensor swarms within fracture networks. Understanding the physics of sensor swarm distributions in fracture networks will have important implications for the future use of collaborative sensors to characterize the subsurface. Our research objectives are: (1) to explore the maintenance and control (hydrodynamic, electro-kinetic, magneto-kinetic) of particle swarms and to identify the key features of the fracture, fluids, particles and control mechanisms that affect swarm transport in fractures; and (2) to determine the best seismic imaging modality (e.g. P-S converted modes) for identifying scattered wave field phenomenon caused by fractures, fracture intersections, matrix anisotropy and non-uniform immiscible fluid distributions in fractures to enable the best sensor swarm release strategies in fracture networks.

FY 2014 HIGHLIGHTS

Contrary to theories for drag on a particle adjacent to a wall, there exists an optimal range of fracture apertures where swarm bifurcations are suppressed and swarms travel farther and faster than outside of this range. In this optimal range, the fracture surfaces maintain the swarm density through confinement that prevents expansion of the swarm and maintains the speed of transport. Experiments were performed to determine the effect of particle size, fluid viscosity and boundary conditions on enhanced transport of swarms in fractures. Enhanced swarm transport in the optimal range is unaffected by (1) bead size distribution (mono- vs poly- dispersions) and (2) a 100x increase in fluid viscosity. An increase in viscosity shifted the optimal range from 2.5 - 15 fracture aperture/swarm diameter ratios to 10 - 20. Local swarm behavior is affected by the resistance to flow in a fracture. When a fracture is confined (no flow boundary conditions), swarms did not exhibit enhanced transport. Enhanced transport only occurs in a fracture that is partially unconfined. Fracture intersections are a major difference between working with single fractures and orthogonal fracture sets. A theoretical and experimental study was performed to examine seismic wave propagation along a fracture at the surface, i.e., along the intersection of two quarter-spaces. A theoretical model that couples two wedges, using displacement discontinuity boundary conditions, gives rise to a new guided waveform that is dispersive, depends on specific stiffness of the intersection of a fracture with a free surface, and exhibits velocities that range from the single wedge-mode velocity to the Rayleigh wave velocity at a free surface. The existence and behavior of this new guided-mode was verified using a synthetic fracture created between two aluminum blocks. This new guided-mode enables the characterization of fractures, joints and other discontinuities at the surface of an outcrop.

Structural Basis for Stabilization and Transformation Behavior of Amorphous Calcium Carbonate

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Funding: \$78,918 (2014)

PROGRAM SCOPE

Calcium carbonate biomineralization is one of the most important processes in the carbon cycle, and it has been demonstrated that biologic and inorganic formation of calcium carbonate minerals commonly occurs via a metastable amorphous precursor: amorphous calcium carbonate (ACC). A limitation in our ability to integrate the role of ACC into quantitative geochemical modeling is the challenge in evaluating its structural properties, including the distinct types of molecular water in ACC and their role in its stabilization and transformation. Our present research program builds on our previous work combining synchrotron X-ray total scattering methods and NMR spectroscopy by adding the unique capability of neutron total scattering to overcome the poor sensitivity of H for X-rays. Combined with deuterium substitution, neutron total scattering and pair distribution function analysis permit direct evaluation of molecular water components. Parallel NMR experiments that also take advantage of deuterium substitution and employ double resonance techniques will permit assignment of distinct types of molecular water and their functional roles in the stabilization and transformation of ACC. *In situ* transformation studies will allow direct characterization of ACC crystallization kinetics. The structural information obtained in this study will provide a basis for understanding energetic and kinetic differences among varieties of ACC and associated transformation pathways. Structure models that result from this research will be used as a basis for computational modeling that examines structural interactions of ACC with inorganic and organic additives, with templates, and transformation to different crystalline forms of calcium carbonate. A long-term goal is to develop structural data for different forms of ACC that enable their inclusion in quantitative modeling of geochemical processes.

FY 2014 HIGHLIGHTS

The primary accomplishments in this period focused on the *in situ* determination of ACC transformation kinetics and reaction pathways. Transformation kinetics varied according to ACC synthesis method, and transformation pathway was affected strongly by kinetics. Experiments with slower transformation kinetics showed ACC transforming directly to calcite, while experiments with the fastest transformation rates yielded a mixture of calcite and vaterite. In experiments where transformation produced a mixture of phases, the initial crystallization of vaterite and calcite was simultaneous. Transformation of ACC directly to calcite and the simultaneous formation of vaterite and calcite both indicate that vaterite is not an essential precursor phase in the formation of calcite. However, *ex situ* analysis of capillaries long after *in situ* analysis did show a secondary transformation from vaterite to calcite, with slower reaction kinetics than either of the initial crystallization reactions from the amorphous phase. Reactions involving calcite-equilibrated solution and partially dehydrated ACC both correlated with an overall decrease in the transformation kinetics. These effects are attributed to different populations of hydrous components and their distinct structural roles, which is the focus of ongoing work. The *in situ* structural analyses used in this study shed light on the possible controls manipulated by organisms to direct transformation *in vivo* with potential applications for biomimetic synthesis.

Kinetic Isotope Fractionation by Diffusion in Liquids

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Funding: \$206,400 (2014)

PROGRAM SCOPE

The research supported by the DOE Geoscience Program has had three broad goals:

- 1) To use laboratory experiments to document and quantify kinetic isotopic fractionation effects due to particular mass transport mechanisms such as volume diffusion and grain boundary diffusion.
- 2) To use the experimentally derived isotopic 'fingerprints' to infer the dominant transport processes and the extent to which they operated in natural settings such places volcanic systems were melts of different composition were juxtaposed.
- 3) Once chemical gradients in natural settings have been demonstrated to have been the result of diffusion, the length scale of the diffusion is used to place constraints on the cooling history of the system.

FY 2014 HIGHLIGHTS

During fiscal year 2014 we expanded our research documenting the rate of chemical diffusion and associated isotopic fractionation from liquids to silicate minerals and metal alloys. The kinetic isotope fractionation by diffusion in minerals is especially important because different elements (i.e., lithium versus magnesium) diffuse at very different rates in different minerals and thus they can provide constraint on different periods of a system's cooling history. We have completed and published our work on lithium diffusion and isotopic fractionation in pyroxene minerals and have completed a parallel study of lithium diffusion into olivine, which is being prepared for publication. We also completed and published our work on thermal isotope fractionation (i.e. isotopic fractionation of an initially homogeneous silicate liquid by an imposed temperature gradient) and showed that the isotopes of all the major elements of a silicate liquid are isotopically fractionated to an easily resolved degree by a temperature difference of only a few tens of degrees. We completed a series of Fe-Ni interdiffusion experiments and high temperature evaporations of Fe, Ni, and Fe-Ni alloys, and as in the case of silicates, very large isotopic fractionation were found in the diffusion couples and in the evaporation residues. All of the work either directly or as an illustrative analogue system provides ways of discriminating between the various processes responsible for mass transport in condensed systems.

Physics of Channelization: Theory and Observation

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Funding: \$187,000 (2014)

PROGRAM SCOPE

We study the growth of channel networks incised by groundwater flow. Our objective is to quantitatively relate mechanisms and rates of channel growth to the geometry of channel networks. Our investigations involve physical reasoning, mathematical theory, and empirical analysis of real drainage networks. Our empirical work focuses on a hundred-square kilometer channel network located on the Florida Panhandle, where channel incision by groundwater seepage is unequivocal. We also study drainage networks at lower resolution throughout the contiguous United States.

FY 2014 HIGHLIGHTS

Work performed during the current grant cycle has shown, by both theory and observation, that channels growing in groundwater fields bifurcate at a characteristic angle of $2\pi/5 = 72$ degrees. To better understand this result, we have created a family of numerical models in which channel tips grow at a rate and direction determined by the two leading-order terms of an expansion of the groundwater field near tips. When augmented by a bifurcation rule, interesting structures, including logarithmic spirals similar to features seen in the Florida network, are obtained. Our recent work hypothesizes that channel tips grow according to the principle of local symmetry. This concept, adopted from fracture mechanics, suggests that streams grow in the direction in which the groundwater field is locally symmetric. An alternative view, which we previously adopted to predict the 72-degree bifurcation, suggests that tips grow in the direction of the streamline entering tips. By comparing streams grown according to the two different growth laws (both analytically and numerically) we find that the two formulations are equivalent. Moreover, they are equivalent to stating that streams grow in the direction that maximizes flux to tips. Consequently we now have a mathematical interpretation of flux-maximizing growth that can be implemented numerically. We have used such a procedure to reconstruct the evolution of the Florida network and determine how its growth rates scale with the groundwater flux to tips. We have also recently initiated a project in which seek to determine the geographical extent of erosion driven by subsurface flow. Preliminary results suggest that the influence of groundwater seepage on network growth is widespread, and that it is controlled by climatic factors that determine groundwater recharge.

Collaborative Research: Damage and Burst Dynamics in Failure of Complex Geomaterials

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Funding: \$125,000 (2014)

PROGRAM SCOPE

Objectives: 1. Determine the dynamics of failure in complex geomaterials, specifically focusing on the role of defects, damage and asperities in the catastrophic failure processes (now popularly termed “Black Swan events”). 2. Examine fracture branching and flow processes using models for invasion percolation, focusing particularly on the dynamics of bursts in the branching process. 3. Understand the fundamental dynamics of nucleation in complex geomaterials, specifically in the presence of

inhomogeneous structures. We use numerical simulations and theory, together with new classes of models, to obtain answers to the project objectives described above. Modeling these types of processes requires consideration of fully interacting fields of dislocations, defects, damage, and other material disorder. Observations of rock masses over a range of spatial scales indicate that the failure modes of these systems demonstrate scale invariant deformation, or power law behavior. These are observed in both laboratory settings in acoustic emission experiments, as well as in large scale field settings associated with tectonic faults. In much of the previous work over the last decades on these types of systems, disorder fields were assumed to be non-interacting or dilute, allowing classical solid-solid mixture theories to be employed. An important new topic we consider in detail is models of the invasion percolation (“IP”) type. The model has been previously researched for applications of extracting oil and gas from reservoirs, and also in the context of the computation of scaling exponents. Notable among the physical processes of IP is the concept of bursts, defined as rapid changes in the configuration of the percolation lattice. Understanding the dynamics of bursts is critical to illuminating the metastable (nucleation) processes by which natural fracture networks evolve and grow, and from which catastrophic failure originates.

FY 2014 HIGHLIGHTS

Publications this year arising from grant:

1. J.Q. Norris, D.L. Turcotte and J.B. Rundle, Loopless nontrapping invasion-percolation model for fracking, *Phys. Rev. E.*, 89, 022119 (2014).
2. D.L. Turcotte, E.M. Moores and J.B. Rundle, Super Fracking, *Phys. Today*, 67, 34-39 (2014).
3. J.Q. Norris, D.L. Turcotte and J.B. Rundle, Anisotropy in fracking: A percolation model for observed seismicity, *PAGEOPH*, in press (2014)

Electrical and Mechanical Properties of Rocks at the Sub-Millimeter Scale

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Funding: \$139,366 (2014)

PROGRAM SCOPE

Our main scientific contributions have been 1) the development of quasi-optical THz scanning techniques for high-spatial-resolution retrieval of the complex dielectric properties of rocks, whether thin-sections or bulk samples, and 2) The construction of a high-Q THz open cavity resonator, which allows us via perturbation techniques to retrieve the complex permittivity of samples that are too small or low-loss to be feasible in a quasi-optical geometry. We established collaborations with Purdue University (Mechanical Engineering), Colorado School of Mines (Geophysics and Petroleum Engineering), Colorado State University and the National Renewable Energy Laboratory, as a major effort in technology transfer.

FY 2014 HIGHLIGHTS

Main Scientific Results:

- 1) The ability to measure complex dielectric permittivity at sub-100 micron scale. Thus we can produce a high resolution spatial map of mineralogy and other properties derivable from permittivity.
- 2) The ability to measure complex dielectric permittivity of thin films (less than 1 micron).
- 3) This allows us to characterize geologic thin films nondestructively, as well as the kinds of films used in renewable energy such as photovoltaics.
- 4) Application of this technology to characterizing the chemical properties of rocks and fluid filled porous media. This is a joint effort with Manika Prasad's group in Petroleum Engineering.
- 5) Due to the noncontacting nature of the measurements, we can study fluid flow and pyrolysis in real time.

Publications:

- 1) N. Greeney and J.A. Scales, Non-contacting characterizing the electrical and mechanical properties of rocks at the submillimeter scale, *Applied Physics Letters*, 100, 124105, 2012
- 2) Rezwanur Rahman, Douglas K. McCarty, Manika Prasad, and John A. Scales, Sub-THz complex dielectric constants of montmorillonite clay thin samples with Na⁺/Ca⁺⁺-ions. Submitted to *Journal of Geophysical Research* 2014
- 3) R. Rahman, P.C. Taylor and J.A. Scales, A system for measuring the complex dielectric properties of thin films at submillimeter wavelengths with an open cavity and a vector network analyzer *Reviews of Scientific Instruments*, 2013
- 4) Greeney, N.S., K.M. Strovink, J.A. Scales, A.M. Jessop, J. Stuart Bolton, C.C. Watson and D.E. Adams, Non-contacting transfer of elastic energy into explosive simulants for dynamic property estimation, *Journal of Applied Physics*, 2014
- 5) Rhaman, R., T. Ohno, P.C. Taylor and J.A. Scales, Optically activated sub-millimeter dielectric relaxation in amorphous thin film silicon at room temperature, *Applied Physics Letters*, 2014.

Shale Gas: Geochemical and Physical Constraints on Genesis, Storage, and Producibility

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Juergen Schieber; Indiana University
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Funding: \$300,000 (2014-2015)

PROGRAM SCOPE

Shales are important source and reservoir rocks for hydrocarbons (shale gas, oil). The three research goals of this project encompass: (1) Quantification of the character and development of porosity in organic-rich rocks as a function of organic matter content, type of organic matter, thermal maturity, and the degree of compaction; (2) evaluation of the natural outgassing of methane from shales into the atmosphere and its potential contribution to global warming by delivering potent methane greenhouse gas; and (3) testing of shales' ability to generate thermogenic gas (or natural gas via catalysis) at relatively low temperatures (60, 100 and 200°C) and different pressures (ambient, 100 MPa, 300 MPa) over months to years. A variety of porosimetric methods was used to assess macro- meso- and

microporosity in shales. Porosity in shales at low maturity initially diminishes due to ongoing compaction, but incipient thermal cracking at the beginning of the oil window generates new porosity. Further into the oil window, the generation of additional liquid hydrocarbons fills pores and reduces the open pore space available for gas storage. At even higher maturity, secondary cracking and gas generation expels some liquid hydrocarbons from pores and opens new pore spaces for gases. Natural outgassing of shale gas into the atmosphere in the absence of drilling and fracking was evaluated during field work in several states. A naturally occurring spectacular “eternal flame” and associated non-burning shale gas seeps in western New York State mark a gas macroseepage system of dominantly thermogenic origin emanating directly from deep shale source rocks. The hypothesis of catalytic gas generation from shales at low temperatures in the absence of methanogenic microbes is being tested by sterile incubation of shales in the presence of deuterium-enriched waters under different temperatures and pressures.

FY 2014 HIGHLIGHTS

High-resolution chemical mapping of organic matter in macerals and pore fillings (as well as of inorganic components) in shales by novel micro-FTIR techniques proved to be a valuable tool for assessing shales’ microstructure (methodology developed and applied by our PhD student Yanyan Chen; Chen *et al.*, 2013, 2014). The occurrence of shale gas seepages through tectonically-induced conduits proves that strong fluxes and point sources of shale gas can indeed contribute to atmospheric greenhouse gas loading, although much ascending methane seems to be microbially oxidized to carbon dioxide by methanotrophs. This is well demonstrated in limestone caves in Kentucky and Indiana that overlie deeper shales. Our results show that the semi-stagnant air in caves typically contains less methane and more carbon dioxide than in the atmosphere, presumably because methanotrophic microbes are lining the walls of underground gas passageways and intercept hydrocarbons (research project of our PhD student Kevin Webster). The hypothesis of catalytic gas generation from shales at low temperatures in the absence of methanogenic microbes is being tested by sterile incubation of shales in the presence of deuterium-enriched waters under different temperatures and pressures. Experiments by our PhD student Lin Wei last from 6 months to two years due to slow kinetics. Low-temperature methanogenesis is indeed observed from some shales and decreases with increasing hydrostatic pressure.

Chen, Y., L. Dethere Caro, M. Mastalerz, A. Schimmelmann, A. Blandón (2013) Mapping the chemistry of resinite, funginite and associated vitrinite in coal with micro-FTIR. *Journal of Microscopy* 249 (1), 69-81. <http://dx.doi.org/10.1111/j.1365-2818.2012.03685.x>

Chen, Y., A. Furmann, M. Mastalerz, A. Schimmelmann (2014) Quantitative analysis of shales by KBr-FTIR and micro-FTIR. *Fuel* 116, 538–549. <http://dx.doi.org/10.1016/j.fuel.2013.08.052>

Mineral-Fluid Interactions: Synchrotron Radiation Studies at the Advanced Photon Source

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Funding: \$105,392 (2014)

PROGRAM SCOPE

This proposal seeks to develop a fundamental molecular-scale understanding of mineral-water interface processes that control the geochemical transport and cycling of elements in Earth's near-surface environment. Processes of interest (including adsorption/desorption, growth/dissolution, and oxidation/reduction) play a critical role in controlling the bioavailability of nutrients and the sequestering or transport of toxins. The program emphasizes direct molecular-scale observations of fundamental geochemical processes through *in situ* studies at mineral-fluid interfaces. This is done using the unique characteristics of the Advanced Photon Source (APS) at Argonne National Laboratory, where the unprecedented x-ray beam properties available at this 3rd generation synchrotron facility (e.g., beam brilliance, flux, and tunability) allow fundamentally new types of *in situ* experiments of mineral-fluid interfaces to be performed, including the ability to visualize the interfacial structure with sub-Å vertical resolution and <100 nm lateral resolution, with unique elemental and chemical sensitivities, and in real-time. These experiments will (1) help bridge the gap between the actual processes and the idealized conceptual models that are used to interpret field-scale observations, (2) further define kinetics and reaction mechanisms at the atomic scale in key mineral-fluid systems, and (3) provide results that can test computational studies of mineral-fluid interface processes through direct comparison to theoretical results. The emphasis of these studies will be to understand the interrelationships between structural, thermodynamic, and kinetic controls of interfacial processes related to ion adsorption and growth/dissolution processes at mineral-water interfaces.

FY 2014 HIGHLIGHTS

The interaction of monovalent cations with the muscovite-water interface reveal the inter-relationships between the adsorption structure and adsorbed ion distribution through a systematic study of alkali metal cations (Li⁺ through Cs⁺, along with H₃O⁺).

GeoSoilEnviroCARS: A National Resource for Earth, Planetary, Soil and Environmental Science Research at the Advanced Photon Source

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Matthew Newville; Chicago, University of
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Funding: \$840,866 (2014)

PROGRAM SCOPE

GeoSoilEnviroCARS, a national user facility at Sector 13 of the Advanced Photon Source (APS, Argonne National Laboratory), provides earth scientists with access to the high-brilliance hard X-rays from this third-generation synchrotron light source. The research conducted on this sector is advancing our knowledge of the composition, structure and properties of earth materials, the processes they control and the processes that produce them. A variety of analytical techniques are being brought to bear on earth science problems: (1) powder, single crystal and interface diffraction; (2) inelastic X-ray scattering;

(3) X-ray absorption fine structure (XAFS) spectroscopy; (4) X-ray fluorescence microprobe analysis and microXAFS; (6) microtomography; (7) high-pressure/high-temperature crystallography and spectroscopy using the diamond anvil cell; and (8) high-pressure/high-temperature crystallography using the multi-anvil press. Upgrade of the GSECARS sector to a dual canted undulator configuration doubled the available undulator beam time, allowed the upgraded X-ray microprobe to operate in a dedicated station with access to the sulfur K edge, and provided an optimized high energy insertion device for interface/surface and high pressure diffraction. All the available user operations beam time is allocated through the proposal-based, peer-reviewed, APS General User Program. GeoSoilEnviroCARS is jointly supported by DOE – Basic Energy Sciences (Chemical Sciences, Geosciences & Biosciences) and NSF – Earth Sciences (Instrumentation and Facilities).

FY 2014 HIGHLIGHTS

The FY14 GeoSoilEnviroCARS user program involved 647 unique users and 343 experiments were conducted resulting in 120 publications. Science highlights include the following:

- 1) Thermodynamic geochemical modeling and bioreactor experiments showed that bacteria *S. oneidensis* MR-1 can enzymatically reduce elemental sulfur but not goethite (α -FeOOH). The HS– produced subsequently reduces goethite abiotically. Fe(III) reduction in aquifers may thus proceed via elemental sulfur-mediated electron-shuttling pathways. (Flynn, T. M., *et al.*, Science 344, 1039-1042, 2014.)
- 2) Images of drainage experiments at extreme conditions demonstrated that super-critical carbon dioxide invades the pore space in Bentheimer sandstone in a capillary-fingering regime. The data support the applicability of previous micromodel studies and ambient condition experiments in predicting flow regimes occurring during super-critical carbon dioxide injection. (Herring, A. L., *et al.*, Int. J. Greenh. Gas Con. 25, 93-101, 2014.)
- 3) Significant sorption of U onto Savannah River Site wetland sediments was observed at pH 8. The primary oxidation state of U in these oxidized sediments was U(VI). The results suggest that U may be strongly bound to wetland sediments, not only under reducing conditions by reductive precipitation, but also under oxidizing conditions through NOM-uranium bonding. (Li, D., *et al.*, J. Environ. Radioactiv. 131, 40-46, 2014.)
- 4) Synthetic garnet, a promising nuclear waste form, incorporates Ce predominantly in the trivalent state at low substitution levels, while a mixture of trivalent and tetravalent states was observed at higher concentrations. In combination with electronic structure calculations, the spectroscopy results suggest a strategy for designing materials in the garnet system possessing thermodynamically favorable substitution properties for actinides. (Guo, X., *et al.*, Chem. Mater. 26 (2), 1133-1143, 2014.)

Synchrotron X-ray Microprobe and Microspectroscopy Research in Low Temperature Geochemistry

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Funding: \$203,000 (2014)

PROGRAM SCOPE

The project focuses on low temperature geochemistry applications of the X-ray Fluorescence Microprobe on Beamline X26A at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. The microprobe can be used to determine the composition, structure, oxidation state, and bonding characteristics of earth materials with trace element sensitivity and micrometer spatial resolution. The following techniques are available for earth and environmental science research: (1) microfocused X-ray absorption spectroscopy, (2) X-ray fluorescence microprobe analysis, (3) microdiffraction, and (4) X-ray fluorescence computed microtomography. A bending magnet source at the NSLS is used along with Si(111) and Si(311) channel-cut monochromators, dynamically-bent silicon mirrors arranged in a Kirkpatrick-Baez geometry for microfocusing, and silicon-drift and Ge energy-dispersive detectors. Focal spots of 5-10 micrometers (FWHM) are achieved resulting in a gain in flux density of about 1500 over a pinhole of comparable size. Research areas include the geochemistry of toxic metals and metalloids in contaminated sediments and particulates, efficiencies of contaminant remediation strategies, speciation of toxic metals in mine tailings, bio-accumulation processes affecting the distribution of trace toxic metal species in soils, iron valence determinations used to infer the oxidation states of magmatic systems, and mineral surface controls on metal partitioning.

FY 2014 HIGHLIGHTS

- 1) Research on the role of cerium dioxide nanoparticle (NP) surface charge and the presence of natural organic matter (NOM) in determining bioavailability and toxicity to the model soil organism *Caenorhabditis elegans* suggested that environmental transformations (specifically coating with natural organic matter) rendered cerium dioxide NPs significantly less toxic. (Collin, B., *et al.* "Influence of natural organic matter and surface charge on the toxicity and bioaccumulation of functionalized ceria nanoparticles in *Caenorhabditis elegans*." ES&T 48, 1280-1289, 2014.)
- 2) Transformation of 30 nm ZnO manufactured nanomaterials (MNMs) in the presence of different concentrations of phosphate as a function of time and pH was examined using a variety of orthogonal analytical techniques. The data revealed that ZnO MNMs react with phosphate at various concentrations and transform into two distinct morphological/structural phases: a micrometer scale crystalline zinc phosphate phase (hopeite-like) and a nanoscale phase that likely consists of a ZnO core with an amorphous zinc phosphate shell. (Rathnayake, S., *et al.*, "A multi-technique investigation of the pH dependence of phosphate-induced transformations of ZnO nanoparticles." ES&T 48, 4757-4764, 2014.)
- 3) Roasting pretreatment of arsenic-bearing ores was evaluated in a broad context and related to the specific operations at the Giant gold mine, Yellowknife, NWT, Canada. The lack of oxidation of the arsenite in the tailings after 50 years is due largely to arsenite incorporation within the maghemite framework associated with structural vacancies. These results suggest that it is crucial to understand the effect of ore processing on the solid As form before investigating the geochemical response of As-bearing wastes in the environment. (Walker, S., *et al.*, "The effect of ore roasting on arsenic oxidation state and solid phase speciation in gold mine tailings." *Geochemistry: Exploration, Environment, Analysis*; in press, 2014)

Predictive Surface Complexation Modeling

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Funding: \$96,511 (2014)

PROGRAM SCOPE

The proposed research aims to integrate the results of the work of many experimentalists into a theoretical model that can be used to extrapolate experimental studies to provide estimates of surface chemistry for systems not yet studied experimentally and for natural and anthropogenically perturbed systems. Three overall goals include: (1) finish the development of a predictive model for silica adsorption on all oxides, (2) investigate the applicability of a general two-site approach built on the PI's previous studies, and (3) improve theoretical relations for predicting metal and oxyanion adsorption, including an investigation of extending the ETLM to higher temperatures and pressures.

FY 2014 HIGHLIGHTS

The geologic complexity affecting the chemistry of mineral-water interactions in shallow subsurface conditions involves a wide variety of variables. These include a wide variety of minerals, and poorly crystalline precursors to minerals, and a very wide range of aqueous species. My previous studies have shown that surface complexation can be applied in a predictive mode for many of the different types of minerals and mineral precursors. Using the extended triple-layer model (ETLM), the application of Born solvation theory enables prediction of adsorption onto many types of solids. Despite this, the geologic reality is that most near-surface and shallow subsurface waters on the continents are predominantly Ca-bicarbonate-silica waters. Consequently, it is essential to be able to model the chemistry of the mineral-water interface in such waters. Remarkably, there is not much experimental information about how such waters behave at the surfaces of minerals. Recent efforts in the present project have been oriented towards developing predictive surface complexation models to address this issue. One example that was completed shows the surprising effect of an organic acid anion (glutamate) on Ca adsorption on rutile. The surface charge on the rutile is completely reversed at pH values of about 7 to 9 by the adsorption of Ca. Under these circumstances, an organic anion can adsorb strongly when it would normally not adsorb. Experimental results are consistent with this behavior. This type of cooperative effect illustrates the need to account for the chemical and geologic complexity of the mineral-water interface in natural systems.

EARLY CAREER: Defining Fe and H Speciation During Olivine Carbonation Under Highly Reducing Conditions

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Funding: \$150,000 (2014)

PROGRAM SCOPE

The water-rock reaction pathways that occur during the anoxic alteration of mafic and ultramafic rocks are not currently well constrained in either theoretical models or laboratory experiments, particularly at shallow subsurface temperatures below 100°C that occur in many hard-rock aquifers hosted in peridotites, gabbros or basalts. In particular, there are wide discrepancies in the predicted amount of H₂ and/or energy that will be generated through the oxidation of Fe during olivine and pyroxene hydration and carbonation, and ongoing debate about the possible pathways of associated CO₂ consumption. The overarching goal of this DOE EC project is to examine the connections among the geochemical behavior of iron, and the extent of hydrogen, methane or carbonate mineral formation during the aqueous alteration of olivine and pyroxene bearing rocks at near surface temperatures and pressures. We are using an integrated suite of microscale x-ray scattering and spectroscopic techniques to interrogate the reactivity and progressive alteration of peridotites during water/rock interaction. We are also measuring the stable isotope composition (δD and $\delta^{13}C$) of hydrogen, water and methane from our experiments to determine whether the water-rock reaction pathways (including biologically influenced systems) can be detected and interpreted in-situ.

FY 2014 HIGHLIGHTS

We are pursuing several unexpected but significant experimental findings that suggest that substantial mineral-driven CO₂-reduction occurs during low-temperature peridotite hydration, resulting in the production of small molecular weight organic acids, particularly during the alteration of partially-serpentinized rocks. These observations have been derived from water/rock alteration experiments in CO₂-bearing fluids reacting with San Carlos peridotite, Cedars peridotite and Oman peridotite, and we are now testing whether we can observe similar processes in-situ in subsurface aquifers, as well as in further experiments with ¹³C labeled substrates. In water/rock alteration experiments with Oman peridotite, we have also shown substantial generation of molecular hydrogen at temperatures between 55-100°C, and tracked the subsequent consumption of rock-derived hydrogen during reaction with dissolved CO₂. We can identify and localize the key Fe-redox reactions occurring during low temperature serpentinization using synchrotron-based microXRF mapping and Fe XANES microspectroscopy. These x-ray spectroscopic approaches are part of an integrated suite of chemical imaging approaches we have developed that utilize QEMSCAN, hyperspectral Raman imaging and multiple-energy x-ray fluorescence mapping to determine changes in Fe speciation during alteration of ultramafic rocks, and to track the extent of in-situ mineral carbonation. We are also developing a low-temperature H₂ isotopic geothermometer and measuring δD of hydrogen gas produced from water/rock interaction in the presence and absence of CO₂ at near-surface temperature. Comparative isotopic data for H₂ generated during low temperature serpentinization reactions has also been obtained from numerous subsurface H₂ and CH₄ rich hyperalkaline fluids collected from deep wells in Oman peridotite that are undergoing modern water/rock interaction.

Disequilibrium Controls on ¹³C-¹⁸O Bond Order in Carbonate Minerals

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PROGRAM SCOPE

The underlying mechanisms for isotopic disequilibrium in carbonate minerals can be studied using: 1) precipitation experiments that have been carefully designed to study under what conditions disequilibrium isotope signatures are observed, and 2) theoretical modeling of disequilibrium and equilibrium processes using principles of quantum chemistry and molecular dynamics. Clumped isotope geochemistry represents a new research frontier, and has the potential to be a powerful tool in the geosciences. We are examining controls on the occurrence of heavy isotope pairs, or other multiple rare isotope substitutions, in molecules. The development of analytical instrumentation and methods for high-precision measurements of clumped isotope signatures is creating new sets of geochemical tools - geothermometers, biosynthetic signatures, forensic fingerprints. Our work is focused on investigating the underlying mechanisms for isotopic disequilibrium in carbonate minerals. We are building a solid framework from which to interpret clumped isotopic signatures in carbonate minerals from a variety of conditions, which would enable applications to study processes as wide-ranging as oil and gas reservoir development, carbon capture and storage, tectonics, climate change, and biomineralization.

FY 2014 HIGHLIGHTS

We have conducted precipitation experiments, measured samples grown from our precipitation experiments and those samples provided by collaborators at both low and high ionic strength and different growth rates, conducted theoretical calculations, tested kinetic models for isotopic fractionation, and used these results to interpret data from geological samples. Key results include:

- (1) Using witherite precipitation experiments to determine the clumped isotope composition of bicarbonate and carbonate ions in a solution.
- (2) Carrying out MD simulations to predict the isotopic composition of different DIC species to compare with experimental data.
- (3) Quantification of mineral-specific acid digestion fractionation factors.
- (4) Using experimental data for calcite from growth reactors to evaluate the influence of DIC speciation, ionic strength, growth rate, and enzymatic activity on isotope signatures in calcite.
- (5) Determining kinetic trajectories in a multi-isotope space (clumped and oxygen isotopes) using both theory and experimental data, and fingerprinting the occurrence of different processes in natural systems.
- (6) Discovering factors that have the potential to drive disequilibrium clumped isotope and oxygen isotope signatures of carbonate minerals. These factors include solution variables including pH, salinity, and cationic composition, the timescale for DIC equilibration, and reactions at the mineral-solution interface, and mineral growth rate.

Improved Sims Analysis of D¹⁸O and D¹³C in Low Temperature Carbonates

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Funding: \$243,085 (2014)

PROGRAM SCOPE

We are refining techniques for microanalysis of stable isotope ratios at intracrystalline-scale in carbonate minerals by SIMS and applying them to diagenetic cements in the Mt. Simon, Eau Claire, and St. Peter formations of the Illinois Basin. The Mt. Simon and St. Peter sandstones are under active evaluation, including drilling and injection, for their potential to store super-critical CO₂ in deep brine-saturated reservoirs. Objectives include:

1. Improve techniques for accurate and precise analysis of O & C isotope ratios by SIMS using ultra-small beam spots (<10µm).
2. Develop standards necessary for O & C isotope analysis of Ca-Mg-Fe-Mn carbonates by SIMS.
3. Measure O & C isotope growth zoning in individual carbonate cements.
4. Determine the zoning, genesis, and timing of porosity reducing carbonate cements.
5. Test our new “δ¹⁸O-microstratigraphy” model for carbonate, feldspar, and quartz cementation in the Illinois basin. We proposed that δ¹⁸O varies with temperature and depth during burial and that microanalysis of δ¹⁸O can be used to correlate the timing of cements throughout the basin.
6. Collaborate in related studies including: experiments on carbonates and quartz to calibrate O, C, & Si isotope fractionations, APT studies of radiation damage, and studies of biocarbonates.

These studies constrain the timing and distribution of cements and of primary vs. secondary porosity. This information is important for predicting the formation of cements that are layer parallel vs. crosscutting and thus for confinement and size of high permeability reservoirs. Better understanding of genesis and timing of diagenetic cements contributes to larger goals of DOE including: CO₂ sequestration in sedimentary basins, geothermal energy, groundwater resources and remediation, and reservoir properties for oil, gas, and drinking water.

FY 2014 HIGHLIGHTS

We published a new model for genesis of quartz cements and evolution of the Illinois basin (Hyodo *et al.* 2014, Chem. Geol.; Sliwinski *et al.* 2013 Penrose Conf.). Our combined SIMS, EMP, and SEM studies of the Eau Claire (Sliwinski *et al.* 2014 Goldsch. Conf; 2015 AAPG) and St. Peter Fms. (Denny *et al.* 2015 AAPG) reveal consistent growth zoning in diagenetic carbonates and feldspars that conform to patterns established for quartz cements, confirming our model for evolution of the Illinois basin. Two papers are in preparation. We completed experiments to calibrate O and Si isotope fractionation between quartz and water at 275°C (Pollington *et al.* 2013 AGU; paper in review by Pollington *et al.*) We obtained promising specimens varying from dolomite to ankerite and evaluated them as SIMS standards. This required SEM imaging of 67 samples, quantitative chemical analysis by electron probe (22 samples), calibration of O & C isotope ratios by conventional bulk-analysis (15 samples), and detailed stable isotope analysis by SIMS in different sessions for O and C (20 samples/each, 40-50 spot analyses/each). This massive undertaking has yielded 13 standards of dolomite-ankerite. This new calibration demonstrates significant curvature of SIMS bias (IMF) vs. Mg#, showing that studies using pure dolomite as a standard would be in error by up to 8%. A paper is in preparation by Sliwinski *et al.* We completed SIMS studies of cultured foraminifera for O isotopes (Vetter *et al.* 2013 GCA) and C isotopes (Vetter *et al.* 2014 GCA). SIMS data resolve 12-hour growth bands and correlate to Ba & Sr, demonstrating new approaches to study biomineralization and paleoecology. We completed the first atom-probe studies of minerals. The effects of radiation damage are determined at single-atom scale in 4 zircons (Valley *et al.* 2014 Nature Geo.; 2015 Am. Mineral; UW grad-student, Blum *et al.* 2014 AGU).

The Role of Water in Grain Boundary Diffusion

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Funding: \$231,000 (2014)

PROGRAM SCOPE

This project represents a continuing program of experimental research at RPI aimed at furthering our knowledge of chemical transport in the lithosphere, focusing on grain-boundary diffusion of elements that are largely excluded from mineral grains. We are targeting in particular the role of H₂O in grain boundary transport in the absence of a free fluid phase, because field-based studies suggest that trace amounts of hydrous species in grain boundaries increase grain boundary diffusivities by several orders of magnitude. This possibility is significant because the P-T evolution of many solid-Earth systems probably occurred under “moist” but water-unsaturated conditions. Nearly all previous experimental studies of grain-boundary diffusion have targeted either “wet” (free H₂O) or “dry” systems. It is generally believed that the presence of H₂O molecules enhances grain boundary diffusion, but the dependence on H₂O concentration has not been systematically explored. There is also a lack of information on the quantities of excluded diffusants that can be stored in grain boundaries, how the presence of water might affect the temperature dependence (activation energy) for diffusion, and the extent to which different isotopes of the same element might diffuse at different rates. The challenges in this work include: 1) determining the “dry” baseline in diffusion behavior; 2) adding known small quantities of H₂O to grain-boundary diffusion experiments; 3) stabilizing the system against grain-boundary migration and/or grain growth; and 4) understanding the role of lattice diffusion in bulk transport. We have learned to work with excluded elements by developing what we call the “detector-particle” method for grain-boundary diffusion; we are now applying this method, along with more traditional approaches to grain-boundary diffusion of key elements, to determining the influence of H₂O and quantifying any effects of isotope mass on diffusion of geochemically strategic elements.

FY 2014 HIGHLIGHTS

We completed and published an investigation of grain-boundary diffusion of Mg in nominally dry quartzite, obtaining some of the highest grain-boundary diffusivities reported to date. This study involved olivine and pyroxene detector particles dispersed in synthetic quartzite samples for the purpose of “scavenging” Mg from the grain boundaries. This technique enabled us -- in addition to obtaining estimates of grain-boundary diffusivities and activation energies for diffusion -- to show that the partition coefficient for Mg between pyroxene and quartz grain boundaries is remarkably high, probably close to 1. Large quantities of “ghost” Mg (and probably other incompatible elements) can be transported and stored in quartz grain boundaries of this simple analog system. The same conclusion can probably be generalized to more realistic rock compositions. In December, 2014, Veronika Homolova successfully defended her doctoral thesis, which includes chapters on diffusive fractionation of Li isotopes in the grain boundaries of polycrystalline olivine, and also by lattice diffusion in olivine single crystals (characterizing lattice diffusion was necessary to understand bulk diffusion and separate the contribution of grain boundaries). In the Li grain-boundary diffusion experiments, ⁷Li/⁶Li ratios systematically dropped by up to ~6% along ~1-mm long diffusion profiles, indicating that ⁷Li diffuses

significantly more slowly than ${}^6\text{Li}$. Equally large differences in ${}^7\text{Li}/{}^6\text{Li}$ were produced within large single crystals of olivine over distances of only 0.1-0.2 mm. Clearly, both lattice- and grain-boundary diffusion of Li have significant potential to fractionate Li isotopes in natural systems at a variety of scales. This is probably true of higher-Z elements as well, but to a lesser degree because of the proportionately smaller mass difference among isotopes. In polycrystalline samples, most of the diffusive isotope fractionation appears to take place within the grain boundaries.

Anisotropy and Residual Stresses in Sedimentary Rocks: A Synchrotron and Neutron Diffraction Study

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Funding: \$160,000 (2014-2015)

PROGRAM SCOPE

First a major effort is the investigation of elastic anisotropy in phyllosilicate-rich rocks. This is motivated by a need to understand and develop predictive models for the acoustic anisotropy in mudstones and shales. We are analyzing shales from a wide variety of environments to better understand crystal alignment during sedimentation, compaction and diagenesis. Also, sedimentary shales will be compared with fault gouge of similar composition (from the SAFOD project), slates and metamorphic schists, where phyllosilicate alignment was produced by recrystallization. We have relied on synchrotron hard X-ray diffraction, neutron diffraction and X-ray microtomography to quantify crystallite preferred orientation and pore space geometry. Second, we are exploring the *in situ* state of stress by measuring residual stresses that are still present in minerals of deformed rocks by local lattice distortion. This effort will focus on quartz, where we have exciting preliminary results. Experiments are performed with microfocus X-ray diffraction using the Laue imaging technique at the ALS synchrotron. The project provides data that are critical for interpreting macroscopic seismic observations. The methods in synchrotron and neutron diffraction that will be developed, as well as advanced methods of data analysis, are relevant for a broad range of physical sciences. The experimental as well as modeling methodologies that are developed will become available to other researchers and the still very confined texture research will be promoted for a broad range of earth sciences through workshops, training and publication of tutorials.

FY 2014 HIGHLIGHTS

The past year has been very productive, providing exciting new insight about anisotropy and stress patterns in rocks. 11 journal publications describe the results. Below are some highlights. With a newly developed self-consistent averaging method we can now predict anisotropic properties of shales based on microstructure, grain and pore geometry, preferred orientation and volume fractions. The modeling results are in excellent agreement with ultrasonic measurements of wave velocities (Kanitpanyacharoen *et al.* 2013, *J. Syn. Rad.* 20, 1-9; Vasin *et al.*, 2013, *J. Geophys. Res.* 118, 1-26; Vasin *et al.* 2014, *Geophysics* in press; Kanitpanyacharoen *et al.* 2014, *Geophysics* in press). In collaboration with geophysicists at Prague we are developing methods to measure P and S velocities on spheres, which allows complete derivation of the aggregate elastic tensor. Comparison with the microstructurally modeled tensor there is amazing agreement (Wenk *et al.* *J. Geophys. Res.* 2015, submitted). Perhaps

most exciting has been the quantification of stress in quartz from the San Andreas Fault observatory at Depth. Stresses of 300 MPa are still preserved. This will be reported in *Geology* (Chen *et al.* 2015, *Geology* in press). The educational aspect is also important, especially to train users in the sophisticated data analysis. A workshop at ALS in December 2013 attracted a large audience and two publications with tutorials received much attention, including Journal cover pages (Lutterotti *et al.* 2014, *Powder Diffraction* 29, 76-84; Wenk *et al.* *Powder Diffraction* 29, 220-232).

A Detailed Study of the Physical Mechanisms Controlling CO₂-Brine Capillary Trapping in the Subsurface

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Funding: \$145,215 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

Capillary trapping is a somewhat under-explored mechanism in geologic sequestration of CO₂. Central to capillary trapping is its pore-scale nature: pore-scale geometry, fluid velocities, as well as brine- CO₂ interfacial physics will strongly determine the magnitude of capillary trapping. Because of its stable immobilization characteristics, capillary trapping has several advantages over structural trapping; advantages include not being affected by potentially compromised reservoir caprock, facilitating enhanced dissolution of gaseous CO₂ into the brine, and allowing gaseous CO₂ to be distributed over a larger reservoir volume. Compared to most current large-scale reservoir studies, our research takes several steps back in scale to observe and model trapping at the pore-scale and to learn how these findings translate into continuum scale properties that can subsequently support improved modeling of sequestration at large spatio-temporal scales. Two parallel but strongly interacting approaches are followed in our research (DE-FG02-11ER16278 and DE-FG02-11ER16277). The Oregon State University group, under leadership of Dr. Dorthe Wildenschild, conducts x-ray micro-tomography measurements of the capillary trapping process using proxy fluids to explore the effect of varying interfacial tension, viscosity, and flow rate on the resulting trapped amount of CO₂. The group at the University of Arizona, under leadership of Dr. Marcel Schaap, is developing functionality into lattice Boltzmann models that allow for the physical conditions found in the experiments as well as relevant pressure and temperatures found in candidate geological reservoirs.

FY 2014 HIGHLIGHTS

The OSU portion of this research has utilized x-ray computed microtomography to investigate nonwetting (NW) phase fluid movement and trapping on a pore-scale basis. We have utilized both ambient-condition and supercritical condition experiments to focus on three areas of study which are of significant importance to geologic sequestration of supercritical phase CO₂: (1) Variation of wetting (W) and NW fluid/engineering/medium properties and the resulting transitions in pore-scale force dominance; (2) Impact of the post-drainage, initial state of the system on the post-imbibition, residual state of the system; (3) Influence of wettability state on NW phase fluid flow and mobilization. In addition, supercritical-condition CO₂ injection experiments have been successfully conducted and used to relate the results to ambient condition studies to demonstrate the applicability of flow theories and models. The UA portion of the research has focused on 1) optimizing the lattice Boltzmann micro scale

code for computational speed (source code refinements) and implementation of parallelization routines to enable the code to run on high-performance clusters. 2) We found that the segmentation algorithms have huge (orders of magnitude) effect on computed flow rates for porous media obtained with broad spectrum x-ray tomography. 3) Development, parametrization and testing of multi-component equation of states capable of simulating the brine-CO₂ system under reservoir conditions. We found that we are able to reach the large density ratios and interfacial tension ranges required for this project and demonstrated that multiphase conditions (gas/liquid) of both single and multicomponent can be simulated in a stable fashion using numerically inexpensive algorithms.

DOE National Laboratories

Geochemistry of Interfaces: From Surfaces to Interlayers to Clusters

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Funding: \$690,000 (2014)

PROGRAM SCOPE

Mineral-water interfaces provide the critical setting for many geochemical processes in the environment. Surface properties of mineral substrates and the modified behavior of water molecules near the interface relative to bulk water remain difficult to characterize despite the best efforts of modern analytical methods. Although the science of interfacial chemistry has advanced significantly in recent years, there remain significant gaps in our knowledge of structure, reactivity, dynamics, and molecular mechanisms at both mineral surfaces (including the confined interlayers of clay minerals) and nanoscale molecular clusters (that consist predominately of surfaces comprised of oxygen, hydroxyl, and water ligands). This project combines computational, synthetic, and spectroscopic tasks to examine the nature of complex geochemical interfaces. Specific tasks address surface speciation, adsorption phenomena, surface complexation modeling, ion-pairing, interlayer structures, edge-site parameterization for clay minerals, and molecular cluster synthesis. Computational efforts emphasize the use of large-scale molecular dynamics simulations, *ab initio* MD, and related density functional theory and classical methods to address structure and thermodynamics of mineral-water systems. A suite of experimental and spectroscopic approaches are used to complement the computational efforts.

FY 2014 HIGHLIGHTS

We made significant progress in classical force field development for species on the edges of clays using hydrated oxide models. Vibrational frequencies from normal mode analysis of classical models are matched to DFT calculations. We used MD simulation and inelastic neutron scattering to study water vibrational behavior in smectite minerals. We collected INS spectra of hydrated and dehydrated montmorillonite and beidellite at LANSCE at LANL, and recently at the Spallation Neutron Source at ORNL, for samples exchanged with various alkali and alkaline earth cations. We examined organic dye

methylene blue at kaolinite surfaces to assess adsorption and aggregation of large cations on clays. We examined interfaces between goethite (α -FeOOH) and aqueous $MgCl_2$ or $BaCl_2$ solutions using classical MD. Mg^{2+} adsorbs as an outer-sphere complex complete with its hydration shell, and Ba^{2+} adsorbs as outer sphere on the (100) goethite surface and as both inner- and outer-sphere complexes on the (101) surface. These results are consistent with MD results for alkaline earth metal adsorption onto gibbsite ($Al(OH)_3$), but seem inconsistent with bulk adsorption data from UT Austin. *ab initio* MD for (101) goethite determine the energetic viability of the $PbSeO_3$ ion pairs proposed by UT Austin surface complexation models. Integration with data and models from Ohio State & UT is challenging our prior conceptions of the relationship between the strength of metal adsorption and metal solvation. To study the reactivity of the Fe(II)/Fe(III) couple in clay structures, we synthesized pure Fe-phyllosilicate and characterized it using X-ray diffraction, small-angle X-ray scattering, and Mössbauer spectroscopy. The structure and particle geometry of synthetic Fe-phyllosilicate is similar to natural nontronite, but with a lower degree of crystallinity and smaller average particle size. The Fe(II) content in the synthetic Fe-phyllosilicate is about 1-3% of total Fe and free of Fe-oxide impurities.

Integrated Isotope Studies of Geochemical Processes

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Funding: \$765,000 (2014)

PROGRAM SCOPE

Objectives are to better understand (1) molecular to micro-scale processes that control isotopic fractionation and trace element partitioning during mineral precipitation and transport in fluid phases and (2) behavior of isotopes and trace elements in large-scale hydro-geochemical systems. Molecular scale models are developed for mineral formation at both high and low temperatures, using isotopic and trace element fractionation effects as a guide to dynamical processes at the mineral surface. Isotopic fractionation during diffusion in liquids is also studied. Large scale system studies involve development of methods for characterizing transport and fluid-solid reactions rates using isotopes of solid radiogenic elements (Sr, Nd, Pb, Ca, U, etc.), light stable isotopes (O, C, H, Li, N, S, Ca, Mg, etc.), and noble gases (He, Ne, Ar, Kr, Xe). Molecular to micro-scale processes are addressed with experiments and measurements on natural systems focused on Ca, Mg, and O isotopic fractionation and trace metal incorporation during mineral precipitation, isotopic fractionation associated with diffusion of ions in aqueous solution, gases, and silicate liquids, and noble gas incorporation into biogenic and diagenetic minerals. Field scale research includes advancement of geochronological techniques focusing on U-Th-He and groundwater noble gases, studies of noble gases as gas phase partitioning tracers, investigation of S, H, C, and Fe isotopic fractionation during abiotic sulfide reduction, kinetic isotopic effects in pore fluids, sedimentary minerals, and plants, and modeling of isotopic effects due to fracture flow and inhomogeneous permeability in fluid-rock systems.

FY 2014 HIGHLIGHTS

The ion-by-ion growth model for calcite that predicts the variable Ca isotopic fractionation associated with non-equilibrium growth from oversaturated solutions has been extended to account for C and O isotopic fractionation, and also for clumped C-O isotopologues in calcite. The model is based on fits to new experimental data for the dependence of O isotopic fractionation in calcite on temperature, pH and growth rate, which incorporate the use of dissolved carbonic anhydrase in the precipitating solution to ensure isotopic equilibration of dissolved carbonate species. The resulting formulations represent the first comprehensive description of non-equilibrium Ca and O isotopic fractionation into calcite and have broad implications for the use of calcite as a paleoenvironmental proxy. Ca isotopes in calcite were also used to relate CO₂ loss to calcite precipitation during evolution of hydrothermal fluids in an active geothermal system. Experiments confirm models for the transport of noble gases during advection of CO₂ through porous media, and that Fe-oxyhydroxide nanoparticles are especially effective at adsorbing heavy noble gases while excluding light noble gases. Isotopic fractionation of K isotopes by diffusion has been shown with new experiments to be much smaller in methanol than in water, providing additional clues to mechanisms of ionic transport in these fluids.

Geomechanics Research

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Funding: \$553,000 (2014)

PROGRAM SCOPE

Subsurface engineering endeavors, be they waste storage or resource extraction, rely on computational methods and characterization for prediction, risk and performance assessment. Central to these efforts are continuum constitutive models linked to first-principles conservation laws that are then represented in discretized numerical models of ever-increasing complexity. This project fills in knowledge gaps on multiphysics constitutive laws applicable to fluid pressured porous media, including pore-scale structures and topologies that define limits of applicability for traditional Darcy-type flow laws and influence percolation behavior, effective pressure laws that expand from typical Biot poroelastic treatments to include yielding and partially-drained effects, and stress-strain mechanical constitutive laws that move our understanding beyond ad-hoc non-associative elasto-plasticity or soil mechanics approaches. Specific tasks examine the coupling of mudstone mechanical, hydrological and chemical multiphysics as impacted by pore topology and structure, percolation methods that describe multiphase fluid invasion physics and capillary hysteresis, and thermodynamically-constrained mechanical laws validated by experiment. Novel imaging methods guide constitutive law development and include 3D

focused ion beam/SEM, optical and TEM confocal, SEM and TEM-EDS, CT scanning, and ultrasonic/acoustic methods.

FY 2014 HIGHLIGHTS

Central to FY 2014 efforts have been the successful submission of a renewal proposal in February titled “Shale Poromechanics: Heterogeneity, Flow, Failure, and Creep”; this is an outgrowth of this current project and was initiated in early FY 2015. Dewers and Heath along with Bill Carey from LANL received approval for AGU Fall Meeting session titled “Shale Science: Coupled Processes in Hydraulic Fracturing and CO₂ Sequestration.” Heath and Dewers (with A. Ilgen from Sandia) submitted a proposal to LANSCE titled “Deformation Partitioning in Shale Observed with in-situ Small Angle Neutron Scattering” to obtain beam time for clay deformation experiments and initiated novel experiments examining evolution of clay pore structures under *in situ* loading at the LANSCE facilities. Based on these results, Dewers and Heath worked with LANL staff in developing a new high pressure oedometric view cell for use in small angle neutron scattering. Ingraham *et al.* finished a test series on poroelastic effects. Dewers visited Zuleima Karpyn’s CT lab at Penn State and was given a tour and overview of their new micro-CT instrumentation and facility. A new student from NMT (Joseph Grigg) has begun work on nano-characterization and scale-dependence of shale mechanical properties. Ben Rosandick (NMT) successfully defended his thesis on the Mancos shale petrophysics in July.

Molecular Mechanisms of Interfacial Reactivity in Near Surface and Extreme Geochemical Environments

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Funding: \$2,412,000 (2014)

PROGRAM SCOPE

The Basic Energy Sciences (BES) Geosciences Research Program managed at PNNL is designed to advance our fundamental understanding of molecular and microscopic processes that control interfacial reactivity in near surface to extreme geochemical environments. Specific aspects of the research program are focused on 1) unraveling the dynamics of mineral interfacial reactions and the changes induced in mineral surface chemistry by electron conduction/transfer reactions, 2) determining the

molecular/microscopic mechanism resulting in mineral and water film nucleation and growth in geochemical environments including supercritical fluids and, 3) developing new computational approaches for interrogation of reaction mechanisms at mineral and nanoparticles interfaces. The research program provides a fundamental molecular-level understanding of macroscopic mineral-water and more complex rock-water interactions which are critical for accurately predicting the consequences of geologic disposal of the byproducts of energy production activities. Current activities focus on unraveling the influence of surface specific potentials of redox transformations of the iron oxides, understanding the local chemical environment of uranium substituted into iron oxide minerals, examining the role of interfacial strain in mineral nucleation and growth, providing new insights into transformation of metal silicate to metal carbonate minerals in low water high CO₂ fluids, and the development of new computational algorithms for evaluation of molecular mechanisms of reactivity at mineral surfaces which are applicable for use on petascale/exascale computer platforms.

FY 2014 HIGHLIGHTS

The program had many noteworthy accomplishments in FY14. In the area of redox transformations, we calculated electron mobilities in pure and impure goethite crystals using plane-wave DFT+U calculations, which revealed energetically favorable pathways along the double octahedral chains at nanosecond rates. We also published new experimental work on the incorporation of uranium in goethite, which showed that pentavalent uranium was the primary oxidation state of incorporated U, adding to the list of minerals in which pentavalent uranium is stabilized. Time-sequenced atomic force microscopy images of calcite reacted with cadmium chloride solution were used to quantify overlayer growth kinetics and showed that the heteroepitaxial growth of cadmium carbonate proceeds via three different mechanisms depending on the initial supersaturation: advancement of existing steps, nucleation and growth of three-dimensional islands, and nucleation and spread of two-dimensional nuclei. Crystallization of the overgrowth follows a non-classical pathway involving the formation of a surface precursor that is not fully crystalline, whereas high supersaturation favors the formation of crystalline nuclei. We studied the forsterite-wet supercritical CO₂ system using an innovative *in situ* method for infrared spectroscopic titrations of minerals with water in high-pressure fluids. We showed for the first time that Mg-carbonate surface complexes predominate below the threshold for continuous carbonation. The magnesite particles that form are hundreds of times larger than nanometer thicknesses of the adsorbed H₂O films that facilitate the transformation. First principles simulation analysis of x-ray scattering data were performed to identify solution structures of Ca²⁺ and Zn²⁺ as a first step in the development of molecular-level insight into the structure of the solute species. All areas of the program were productive in high-impact peer-reviewed journals.

Mineral-Fluid Interactions: Synchrotron Radiation Studies at the APS

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Funding: \$521,000 (2014)

PROGRAM SCOPE

We seek a fundamental molecular-scale understanding of mineral-water interface processes that control the geochemical transport and cycling of elements in Earth's near-surface environment. Processes of interest (including adsorption/desorption, growth/dissolution, and oxidation/reduction) play a critical role in controlling the bioavailability of nutrients and the sequestering or transport of toxins. This understanding is necessary for the development of robust predictive capabilities associated with the geological disposal of energy byproducts (e.g., sequestration of CO₂, spent nuclear fuel). The program strategy emphasizes direct molecular-scale observations of fundamental geochemical processes through *in situ* studies at ideal mineral-fluid interfaces. This is achieved using the unique characteristics of the Advanced Photon Source at Argonne National Laboratory (e.g., X-ray beam brilliance, flux, and tunability), allowing fundamentally new *in situ* experiments of mineral-fluid interfaces to be performed, including the ability to visualize the interfacial structures with sub-Å vertical resolution and <100 nm lateral resolution, with unique elemental and chemical sensitivities, and in real-time. These experiments will (1) help bridge the gap between the actual processes and the idealized conceptual models that are used to interpret field-scale observations, (2) further define kinetics and reaction mechanisms at the atomic scale in key mineral-fluid systems, and (3) provide results that can test computational studies of mineral-fluid interface processes through direct comparison to theoretical results. This approach will lead to an understanding of the interrelationships between structural, thermodynamic, and kinetic controls of interfacial processes that ultimately control the transport of elements through the near-surface environment.

FY 2014 HIGHLIGHTS

We have made multiple novel observations of mineral-water interfaces.

- The interaction of monovalent cations with the muscovite-water interface reveal the interrelationships between the adsorption structure and adsorbed ion distribution through a systematic study of alkali metal cations (Li⁺ through Cs⁺, along with H₃O⁺). Specifically, these studies revealed the significant differences in the adsorption energy due to differences in the cation adsorption speciation (i.e., the number of water layer separating the cation and the surface). Observations with Y³⁺ reveal that the large trivalent ion charge of Y leads to a phenomenon of cation “over-compensation” and a broad distribution indicative of multiple coexisting adsorption states.
- Pb²⁺ interaction with the calcite-water interface revealed a distinct interaction with carbonate surfaces. Our results revealed that Pb²⁺ does not interact with calcite by adsorbing on top of the surface, but instead by incorporating within the top 3-4 calcite layers, substituting for the Ca²⁺ ions. This observation was unexpected since the PbCO₃ adopts the aragonite structure in the bulk.
- The initial orthoclase (001) dissolution rates as a function of temperature and pH within the acidic regime (0 < pH < 3.4) was observed revealing two distinct regimes in its systematic variation with pH. Comparison of these results to predictions of transition states obtained by high level theory showed that this behavior could be explained as due to the presence of two distinct reaction sites (i.e., the Al-O-Si vs. the Si-O-Si sites) leading to a change in the rate limiting dissolution process near pH 0.5. We have also made advances in developing the X-ray reflection interface microscopy technique that was first demonstrated in this program. Recent advances include changes in optics that provide shorter imaging times as well as an improved spatial resolution of 70 nm.

Interconnections Between Dynamic Processes That Control the Formation, Evolution and Reactivity of Environmental Interfaces

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Funding: \$1,612,000 (2014)

PROGRAM SCOPE

Objectives are to better understand (1) molecular to micro-scale processes that control isotopic fractionation and trace element partitioning during mineral precipitation and transport in fluid phases and (2) behavior of isotopes and trace elements in large-scale hydro-geochemical systems. Molecular scale models are developed for mineral formation at both high and low temperatures, using isotopic and trace element fractionation effects as a guide to dynamical processes at the mineral surface. Isotopic fractionation during diffusion in liquids is also studied. Large scale system studies involve development of methods for characterizing transport and fluid-solid reactions rates using isotopes of solid radiogenic elements (Sr, Nd, Pb, Ca, U, etc.), light stable isotopes (O, C, H, Li, N, S, Ca, Mg, etc.), and noble gases (He, Ne, Ar, Kr, Xe). Molecular to micro-scale processes are addressed with experiments and measurements on natural systems focused on Ca, Mg, and O isotopic fractionation and trace metal incorporation during mineral precipitation, isotopic fractionation associated with diffusion of ions in aqueous solution, gases, and silicate liquids, and noble gas incorporation into biogenic and diagenetic minerals. Field scale research includes advancement of geochronological techniques focusing on U-Th-He and groundwater noble gases, studies of noble gases as gas phase partitioning tracers, investigation of S, H, C, and Fe isotopic fractionation during abiotic sulfide reduction, kinetic isotopic effects in pore fluids, sedimentary minerals, and plants, and modeling of isotopic effects due to fracture flow and inhomogeneous permeability in fluid-rock systems.

FY 2014 HIGHLIGHTS

The ion-by-ion growth model for calcite that predicts the variable Ca isotopic fractionation associated with non-equilibrium growth from oversaturated solutions has been extended to account for C and O isotopic fractionation, and also for clumped C-O isotopologues in calcite. The model is based on fits to new experimental data for the dependence of O isotopic fractionation in calcite on temperature, pH and growth rate, which incorporate the use of dissolved carbonic anhydrase in the precipitating solution to ensure isotopic equilibration of dissolved carbonate species. The resulting formulations represent the first comprehensive description of non-equilibrium Ca and O isotopic fractionation into calcite and have broad implications for the use of calcite as a paleoenvironmental proxy. Ca isotopes in calcite were also used to relate CO₂ loss to calcite precipitation during evolution of hydrothermal fluids in an active geothermal system. Experiments confirm models for the transport of noble gases during advection of CO₂ through porous media, and that Fe-oxyhydroxide nanoparticles are especially effective at adsorbing heavy noble gases while excluding light noble gases. Isotopic fractionation of K isotopes by diffusion has been shown with new experiments to be much smaller in methanol than in water, providing additional clues to mechanisms of ionic transport in these fluids.

Nonlinear Elasticity in Rocks

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Funding: \$230,000 (2014)

PROGRAM SCOPE

Unraveling the physics of an earthquake's source, reliable sequestration of CO₂, predicting wellbore breakout in oil and gas reservoirs, monitoring and imaging hydraulic fracture, monitoring thermal damage to rock in nuclear waste storage, and probing rock and cement integrity are all areas of research that require a new approach to material characterization and imaging. A material's elastic nonlinear response is extremely promising in this regard, and as far as we know, there is no more sensitive measure of material mechanical damage. A persistent problem in the application of nonlinear diagnostic imaging methods has been the direct relation between elastic nonlinearity and mechanical damage, because a physics-based theory does not yet exist; however, recent work has led to an experimental breakthrough in measuring material nonlinear response. The breakthrough, termed dynamic acousto-elasticity (DAE), has significant implications for the development of a physics based theory, and thus ultimately to our ability to quantitatively relate nonlinear response to material damage. In order to address the question of the origin of elastic nonlinearity in a material, we are developing DAE in conjunction with a new theoretical approach based on an extended Arrhenius model in combination with a numerical modeling approach based on local interactions. The outcome of this work will be a major advance in the domain of nonlinear mesoscopic elasticity research, and will have importance to OBES interests in wellbore collapse, near wellbore fracture conduits, CO₂-induced mechanical changes and general rock and cement integrity studies.

FY 2014 HIGHLIGHTS

During the past year we had a significant breakthrough in our understanding of the nonlinear elastic parameters that are measured applying Dynamic Acousto-Elasticity (DAE). We measure five different signatures of nonlinearity applying DAE; however we find that we need only measure two of them in order to fully characterize the nonlinearity (assuming a homogeneous, isotropic effect). This simplifies the experimental work and the theoretical approach considerably. This breakthrough is described an article that is currently in press in the Journal of Geophysical Research. We also had a breakthrough in application of DAE. We hypothesize that DAE can be applied to characterize the strong ground motion response of a site of interest. In this case we conducted an experiment in west Texas applying a large vibrator source to excite the nonlinear elasticity of the sediments, and we probe with accelerometers mounted in boreholes. We find that the site can be fully characterized in an advanced manner compared with other techniques and that the method holds great promise to future applications. This work was published in the Journal of Geophysical Research this year. A follow on experiment was conducted at Los Alamos this year as well applying a modified version of the experimental configuration. Analysis is in progress. The theoretical work that should provide the means to obtain the causal scale of

the features responsible for the nonlinear response is advancing as well, and it is a challenging problem. Initial results were published this past year by collaborators in Colorado and Russia. Our work involves collaboration with the University of Texas at Austin, with the Laboratory of Parametric Imaging, University of Paris VII [Sorbonne], with the Institute of Applied Physics, Nizhny Novgorod [Russia], and with the University of Colorado at Boulder.

²³⁰Th-²³⁸U Disequilibrium Measurements

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Funding: \$230,000 (2014)

PROGRAM SCOPE

Uranium-series geochemistry and geochronology techniques have a wide range of applications in a number of fields including hydrology, paleoclimatology, paleoceanography, and volcanology. Our project aims to use well established bulk measurement techniques such as MC-TIMS and MC-ICPMS along with new high spatial resolution LA-MC-ICPMS techniques for U-series measurements. We then apply these techniques to better understand U-series environmental transport and develop/apply U-series chronometers in support of basic geoscience research for energy and waste concerns. Our project has contributed to a 'new wave' of analytical development within the isotope geochemistry community while providing new constraints on actinide mobility. We proposed to, 1) continue development of micro analysis methods for actinide studies, 2) use bulk measurement techniques such as MC-TIMS and MC-ICPMS along with new high spatial resolution femtosecond laser ablation techniques to measure U-series transport in U-rich fractures, 3) investigate near surface transport of anthropogenic and natural components in soil cores, and 4) demonstrate *in situ* methods for uranium-series geochronology of corals. Our work during this project has mainly focused on the first two goals. This work has contributed to our understanding of the geochemistry of mineral-water interactions and assessment of radioactive waste repositories, along with other hydrologic and geochemical processes. Development of high spatial resolution techniques also has applications to human evolution, plate tectonics, forensics and climate change. Finally, the new methods, new understanding, and newly trained researchers that result from this work have contributed to interests of other agencies such as environmental monitoring and threat reduction.

FY 2014 HIGHLIGHTS

Studies of U-series disequilibria near uranium deposits can provide valuable information on the timing of actinide mobility over a range of spatial and temporal scales. In our most recent work (Denton *et al.*, 2013), we characterized the geochemical evolution of the Nopal I uranium ore deposit (Sierra Peña Blanca, Chihuahua, Mexico) in terms of mineral-fluid interactions as well as the role that vertical fractures play in U transport and retention. The Nopal I deposit is a possible analog for actinide transport from a nuclear waste repository in fractured, unsaturated tuff and an arid climate. Samples were obtained from a vertical drill core (PB-1b) that extends to ~250 m depth below the surface. Our data show that uranium concentrations range from ~0.1- 0.8 wt. % and U/Th weight ratios range from ~50-700. The ore deposit contains ~0.57 wt. % U, therefore our results suggest that U has been mobile

up to 200 m depth in the past. $^{234}\text{U}/^{238}\text{U}$ activity ratios in the drill core samples range from 0.66 to 2.44 and illustrate a complex evolution consistent with interaction between groundwater enriched in ^{234}U and a tuff matrix that is depleted in ^{234}U due to recoil-related leaching. Closed-system U-Th model ages are generally >200 ka, and U-Th whole rock isochrons yield ages >200 ka with one exception. Although mineral-fluid interaction is ongoing and more complex open system models are possible, the most consistent interpretation of these data is that the drill core samples have generally remained closed with respect to U and Th mobility for >200 ka. These results confirm our prior U-series chronology studies of surface fractures at this site and provide one indicator of the effectiveness of natural barriers to actinide transport in this type of environment over long (10-100 ka) timescales. The results also provide a baseline for more detailed mineral work on actinide mobility and retention using LA-MC-ICPMS.

Geophysics - Detection and Monitoring of Fluids, Faults and Coupled Processes in the Earth's Crust

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Funding: \$1,152,000 (2014)

PROGRAM SCOPE

The problem we address is how to monitor fluid movement in the Earth using changing geophysical signals (time-lapse seismic and EM data) and to extract from the geophysical data 3D images of the evolving hydrogeological (permeability and porosity) and geomechanical (damage and rock-frame strength) fields. A host of subsurface energy and environmental priorities involve the injection or extraction of fluids from the Earth including CO₂ sequestration, geothermal energy generation and enhanced oil recovery. There is a critical need at present to have 3D time-lapse images of where the fluids go in the subsurface and what they do in terms of fracturing or changes to the rock properties. The work is divided into three focus areas: (1) Rock physics modeling that develops and experimentally tests new models for how changing fields related to fluid injection (fluid pressure, fluid saturation and fracture density) influence geophysical properties such as seismic velocities and electrical conductivity; these relations are the key that allow the evolving fluid invasion process to produce changes in geophysical signals (seismic and EM). (2) Hydrogeological and geomechanical forward modeling that develops novel ways to numerically simulate the complex processes of immiscible fluid invasion and the arrival of cracks and fractures; the proper physical modeling of these processes remains ongoing fundamental research. (3) Inverse modeling that develops various approaches to obtain information about the evolving hydrogeological fields and geomechanical damage from time-lapse seismic and EM data, including seismicity (earthquake) recordings. In the initial time period of FY 2014-2016, the focus is on developing the needed theoretical and numerical modeling abilities to perform this inverse problem with the various components (rock physics and forward modeling) constrained by lab experiments. The initial focus is on applying the developed algorithms to synthetic data sets.

FY 2014 HIGHLIGHTS

We began with the problem of injecting a fluid having a different salinity than the ground water. The injected fluid causes changes to the rock properties through three effects: (1) direct fluid substitution (the injected fluid has a different bulk modulus, viscosity, density and electrical conductivity compared to the *in situ* fluid), (2) fluid pressure-induced changes to the rock frame (permeability, porosity and drained elastic moduli) and (3) the creation of any cracks and fracture damage. A novel finite-difference code was written from scratch that models the above processes with the exception of damage modeling. A novel damage-modeling algorithm was developed that is based on the conservation of energy; namely, new fractures arrive when the work expended in creating new surface area in rocks is just balanced by the reduction in stored elastic strain energy. In the forward modeling of an injected fluid having a different salinity than the *in situ* fluid, we addressed the nature of the fundamental laws controlling the diffusion and dispersion of the solute in porous media and discovered that the transport law for dispersion is not symmetric due to advection. We also developed a way to track the arrival times of a salinity front with the goal of ultimately performing tomographic inversion for the dispersion and permeability coefficients. In other work, we continued to develop an alternative damage model based on the fluid creating wing crack extensions from pre-existing flaws in the rocks. Novel inversion methods were also developed for obtaining seismic moment tensors (that characterize the displacement across slip surfaces) associated with fluid-induced earthquakes; the novelty is to model the entire seismic recording (amplitudes and arrival times) and invert not only for the moment tensor of each earthquake event but for the seismic velocities of the crust using techniques developed by the group for the full-waveform seismic inverse problem.

Mineral Transformations in Supercritical CO₂-Dominated Fluids: Impact on Caprock Integrity

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Funding: \$77,000 (2014)

PROGRAM SCOPE

This project led by Pacific Northwest National Laboratory aims to understand the physical and chemical processes taking place at mineral surfaces in contact with carbon dioxide (CO₂) plus water mixtures and in hydrous carbonates. The project addresses fundamental science questions relevant to the long-term caprock integrity of carbon sequestration sites. The ORNL-led part of this project is focused on the study of the pristine and reacted minerals (e.g., olivine, muscovite) and the properties of sorption phase formed at the mineral grain surfaces. Neutron scattering experiments, primarily neutron diffraction, of minerals (i.e., phyllosilicates, orthosilicates, and hydrated carbonates) are carried out to resolve the structural details of mineral-CO₂ interactions. The second subtask studies the sorption from mixtures of CO₂ and water (D₂O) to pristine and reacted mineral surfaces. The goal of this small angle neutron scattering study is to measure the density and composition as well as the volume (thickness) of the sorption phase for different conditions of temperature and fluid mixture composition. The combined analysis of neutron scattering and sorption analysis data will feed into new models for quantitative description of the sorption behavior of binary mixtures at mineral surfaces. The third subtask studies the structure of hydrated carbonates using neutron diffraction techniques with isotope substitution. The

ORNL effort will be synergistically linked to the overall project, leading to a novel understanding of complex geo-fluids in natural environments.

FY 2014 HIGHLIGHTS

In this project, led by PNNL, neutron scattering, optical spectroscopy, and gravimetric excess sorption measurements are utilized to assess the chemical stability, adsorptive capacity and swelling/shrinking properties of clays upon exposure to CO₂ as a function of pressure, temperature, and water/brine saturation. Neutron diffraction data are currently being analyzed to understand the impact of cation identity on the interlayer spacing, CO₂ uptake, and carbonate formation in smectites and illite. We have performed a quasi-elastic neutron scattering study of the dynamic properties of water in the clay interlayers for different clay hydration states and pressures of CO₂. The observed changes in the water single molecule dynamics are tentatively attributed to mobilization of interlayer water by addition of CO₂. We speculate that the CO₂ may partially substitute for interlayer cation hydration waters, effectively liberating these water molecules from their binding sites. A related FTIR study carried out with researchers at Virginia Tech and NETL measured CO₂ and water accommodation in the clay interlayers at different CO₂ pressures and provided clear evidence against carbonate formation in the clay interlayers. Excess sorption measurements of light hydrocarbon adsorption to clays and shales are currently being performed using the new high-pressure Rubotherm apparatus. In an extension of our ongoing studies of aqueous CO₂ – rock interactions, we aim at identifying the loci of wet natural gas adsorption in shaley rocks. Finally, the properties of hydrated carbonates have been studied by a combination of neutron diffraction and computer modeling. In the first experiments, the atomic to nanoscale structure of deuterated dypingite was measured at the POWGEN diffractometer and combined analysis with high-resolution XRD data is currently underway. Additional studies of other hydrated carbonates are planned to understand the formation and stabilities of these complex minerals.

Geochemical Equilibria and Reaction Dynamics: Atomic- To Pore-Scale Processes

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Funding:	\$1,544,000 (2014)

PROGRAM SCOPE

The long-range goal of this project is to attain a fundamental, quantitative, and ultimately predictive understanding of geofluid speciation, mineral-fluid interfacial equilibria and dynamics, mineral reactivity, and the effect of these properties on the evolution of porous geologic media over wide ranges of temperature, pressure, composition and spatio-temporal scales. There currently exists a major gap in the geochemical community's ability to apply insights gained from integrated experimental and computational breakthroughs at atomistic-molecular scales to pore- and reservoir-scale geochemical processes. In this project our focus is on building a bridge across this gap by developing chemically-

realistic and experimentally guided and validated conceptual and computational models of geochemical reactions and mineral-fluid equilibria, and testing their ability to explain and ultimately predict the complex processes controlling geofluid properties, sorption, mineral growth and dissolution, and the interplay of these phenomena with diffusive/advective transport and nanoconfinement in porous geologic media. We address our project goal in three highly interactive subtasks that will ultimately unleash the ever-expanding power of integrated experimental, computational and analytical methodologies to achieve fundamental and predictive understanding of: geochemical reaction equilibria (Subtask 1); rates of mineral growth and dissolution (Subtask 2); and the textural and mineralogical evolution of porous geologic media resulting from fluid-rock interactions (Subtask 3).

FY 2014 HIGHLIGHTS

Our CMD Gaussian Charge Polarizable Model of water has been expanded to include aqueous electrolytes and their interactions with minerals. We have developed “best practices” to calibrate and validate CMD force fields using geochemical data of thermodynamic, structural and kinetic properties. CMD simulation results were validated by quasielastic neutron scattering data for the diffusional dynamics of water sorbed on minerals. We have measured the structure and vibrational dynamics of the interfacial water on cassiterite nanoparticles using inelastic neutron scattering and neutron diffraction coupled with CMD and *ab initio* molecular dynamics (AIMD), demonstrating the importance of sorbed water in nanoparticle stabilization, aggregation and growth. We expanded the model developed for calcite precipitation to an isostructural mineral containing a cation of substantially slower solvent exchange rate, magnesite. The difference in cation resulted in changes in the relative rates of the crystallization beyond that of just the difference in the solvent exchange rates. We incorporated the number of reactive sites on the mineral surface into the model and predicted net crystal morphologies from measurements of the growth rates of individual crystal faces. We used AIMD to identify the likely surface reactions that limit dissolution of quartz, demonstrating that chloride and alkali cations can promote formation of intermediate species controlling the dissolution process, and validated the simulations with X-ray reflectivity. Neutron scattering was employed to characterize porosity and pore morphology changes due to precipitation in pores during basinal brine migration, weathering, and metamorphic or diagenetic maturation in representative geologic formations. In addition, we have compared the diagenetic evolution of pore structures in tight gas shales as a function of shale composition, and determined that nanoporosity not associated with organic maturation is significant.

Heavy Element Chemistry

Institutions Receiving Grants

Differentiating Between Lanthanides and Actinides

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Funding: \$640,000 (2013-2016)

PROGRAM SCOPE

A break in periodicity occurs in the actinide series between plutonium and americium as the result of the localization of 5f electrons. The subsequent chemistry of later actinides is thought to closely parallel that of lanthanides in that bonding should be ionic and complexation should not substantially alter the electronic structure of the metal ions. Herein, we demonstrate that ligation of californium(III) by a pyridine derivative results in significant deviations in the properties of the resulting complex with respect to that predicted for the free ion. We expand on this by characterizing the americium and curium analogs for comparison. These phenomena are also probed using quantum chemical calculations that support the involvement of 5f, 6d, and 7s orbitals in bonding. We show that these pronounced effects result from a second transition in periodicity in the actinide series that occurs, in part, because of the stabilization of the divalent oxidation state.

FY 2014 HIGHLIGHTS

This work was highlighted as the top discovery of 2014 by the Royal Society of Chemistry

Polymer-Supported Complexants: Metal Ion Selectivity and the Variables of Rational Design

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Funding: \$145,000 (2014)

PROGRAM SCOPE

Polymer-supported complexants are important to environmental remediation, catalysis, separations, and the energy-efficient purification of product streams in industrial processes. The scope of this research is to probe the parameters that lead to a rational design of polymer-supported complexants. Rational design is the *a priori* approach to preparing a complexant that has a high affinity for a targeted metal ion. The parameters most important to the design of polymer-supported complexants are characteristic of the ligand (polarizability and conformational rigidity), metal (polarizability, ionic radius

and geometry) and polymer (conformational rigidity and polarity). The emphasis is on polarity / polarizability since it is present in all three components. The polymer support is polystyrene; rigidity is varied by the crosslink level and polarity is varied with comonomers. A range of metal ions is studied based on differences in polarizability and includes the uranyl ion because of its importance to DOE. A new set of phosphorus-based ligands with ion-exchange and neutral coordinating sites are being prepared, including phosphates, aminoalkylphosphonates and phosphinates. The ligands have different polarizabilities at the binding site due to substituents on and around the phosphoryl group. Monoprotic phosphates bound to ligands capable of metal ion coordination are of interest due to the possibility of synergism. Distribution coefficients are determined and correlated with parameters of the ligand, ion, and polymer. Spectroscopic analysis will give a detailed analysis of ion-ligand interactions. Changes at the binding site before and after loading with metal ions are followed with FTIR and the magnitude of band shifts correlated with the ion – ligand interaction. The goal, then, is to use correlations to define a set of principles wherein it is possible to predict the structure of a ligand that will have the highest affinity for a targeted metal ion.

FY 2014 HIGHLIGHTS

- A new polymer with a high affinity for the uranyl ion was prepared by binding pentaerythritol (PE) to polystyrene. The hydroxyl groups were first converted to bromide to provide a handle on which an array of ligands can be bound. Diethylamine was bound to the PE; greater affinity of the aminated polymer for the uranyl ion is found relative to a polymer with amine ligands directly bound to polystyrene. (Alexandratos, S.D.; Zhu, X. *J. Appl. Polym. Sci.*, 2013, 127, 1758)
- The polarizabilities of four ligands on polystyrene (phosphorylated ethylene glycol, ethylene glycol, sulfonic acid, and dimethylamine) were evaluated with Au(III) and Eu(III). Interactions were followed by percent sorption, acid concentration effect and FTIR spectra. The phosphoryl oxygen, hydroxyl OH, and amine have an affinity of Au(III) > Eu(III) while the sulfonic acid shows Eu(III) > Au(III) indicating neutral oxygen is soft while anionic oxygen is hard. (Zhu, X.; Alexandratos, S.D. *React. Funct. Polym.* 2014, 81, 77)
- In an important advance for the purification of wet process phosphoric acid, polymer-bound monoprotic phosphate ligands were developed for sorption of U(VI) from 3M phosphoric acid. The ligands are new phosphorylated mono- and triethylene glycol esters. The binding mechanism was probed by comparing their results to analogous diethyl esters. U(VI) was sorbed more efficiently by the monoprotic ligand. (Zhu, X.; Alexandratos, S.D. *Chem. Eng. Sci.* in press)
- Hydroxyapatite (HAP) is an inexpensive inorganic polymer made from lime. Its functionalization with ion-selective ligands would provide a low-cost option for environmental remediation. Functionalization with an organic complexant was developed as was a method to determine the amount of organic and inorganic phosphorus in the modified HAP. An increase in organic P capacity and a decrease in inorganic P capacity with increasing reaction time was found. (Daniels, Y.; Zhu, X.; Alexandratos, S.D. *Microchemical J.* 2013, 110, 263)

Thermochemistry and Reactivity of Atomic and Molecular Actinides

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Funding: \$478,000 (2014-2016)

PROGRAM SCOPE

These studies will contribute to understanding the reactivity, thermochemistry, and electronic structure of actinides. Quantitative experimental thermodynamic information for a variety of molecules containing the 5f elements, thorium and uranium, will be obtained. Studies will include reactions of 5f elemental cations with atmospheric gases yielding the thermochemistry of small covalently-bound molecules (such as oxides, carbides, nitrides, and hydrides), as well as ligation enthalpies of the elemental ions and their oxides by water and other ligands. Such quantitative information will be directly useful in the fundamental understanding of the chemical and physical properties of these elements at high temperature and will allow evaluation of chemistries useful in separations technologies. These studies will also provide benchmark data against which advances in electronic structure calculations for these elements can be rigorously tested. Such comparisons will be provided both in house and by collaboration with Dr. Wibe (Bert) A. de Jong, Lawrence Berkeley National Laboratory, an expert on coupled cluster approaches (both single and multi-reference) with relativistic corrections. Guided ion beam tandem mass spectrometry will be used to examine the kinetic energy dependence of a variety of reactions involving 5f-electron metal, metal oxide, and metal fluoride cations. Reactions of these ions with typical atmospheric gases (N_2 , O_2 , CO_2 , and H_2O) and halide containing species will be investigated. Analysis of endothermic exchange reactions using well-developed methods will yield quantitative bond energies of covalently-bound ligands. Binding energies of ligands non-covalently bound to the f-electron metal ions and their oxides will be measured using energy resolved collision-induced dissociation. Ligands could include H_2O , alcohols, ethers, ketones, amines, and more complicated ligands.

FY 2014 HIGHLIGHTS

The reaction of Th^+ with CH_4 (CD_4) and the collision-induced dissociation (CID) of $ThCH_4^+$ with Xe have been studied using guided ion beam tandem mass spectrometry. At low energies, Th^+ reacts with methane to yield $ThCH_2^+ + H_2$ as the only product, with an energy dependence that inconsistent with a barrierless exothermic reaction, as concluded from previous experiments at thermal energies. At higher energies, ThH^+ is the dominant product with $ThCH_3^+$ having a similar threshold energy. The latter product decomposes at still higher energies to $ThCH^+$. CID of $ThCH_4^+$ yields atomic Th^+ as the exclusive product, which indicates this species has a $Th^+(CH_4)$ structure. All cross sections are modeled to provide 0 K bond dissociation energies (in eV) of $D_0(Th+-H) \geq 2.25 \pm 0.20$, $D_0(Th+-CH) = 6.19 \pm 0.16$, $D_0(Th^+-CH_2) \geq 4.54 \pm 0.09$, $D_0(Th^+-CH_3) = 2.60 \pm 0.30$, and $D_0(Th^+-CH_4) = 0.47 \pm 0.05$. Quantum chemical calculations at several levels of theory explore the potential energy surfaces for activation of methane by Th^+ and the effects of spin-orbit coupling are carefully considered. The barrier to the dehydrogenation reaction is thought to exist as a result of the mixed (4F,2D) electronic character of the Th^+ $J = 3/2$ ground level combined with extensive spin-orbit effects. Reactions of Th^+ with H_2 , D_2 , HD , D_2O , and CO have also been studied. Reactions with the isotopomers of dihydrogen yield $D_0(Th+ H) = 2.46 \pm 0.07$ eV. Reaction with D_2O forms ThO^+ (75%) and $ThOD^+$ (25%) with a 70% efficiency at low energies. ThD^+ is also formed at higher energies. The primary ThO^+ and $ThOD^+$ products undergo subsequent exothermic reactions to form both ThO_2^+ and ThO_2D^+ . Cleavage of the very strong CO bond, $D_0(C-O) = 11.1$ eV, can also be induced by Th^+ to form ThO^+ and ThC^+ . Preliminary analysis of these data suggest $D_0(Th+ O) = 8.4 \pm 0.3$ eV and $D_0(Th+ C) = 4.4 \pm 0.3$ eV. The former value lies within the combined experimental uncertainties of the literature value, 8.74 ± 0.26 eV.

Computational Studies of NMR and EPR Parameters for Molecules Containing d- and f-Elements

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Funding: \$140,000 (2014)

PROGRAM SCOPE

Actinide (5f) and lanthanide (4f) complexes have fascinating chemical and physical properties but they are not understood sufficiently well. Since actinides constitute dangerous radioactive and toxic components in nuclear waste there is an urgent practical need to address this problem. Theory is an integral part of the solution to this problem. We investigate magnetic properties of 4f- and 5f-element compounds (lanthanides, actinides) by using quantum theory and quantum chemical calculations. The main objective is to learn how observable magnetic properties are related to the geometrical structure, chemical bonding, and the nature of the ground and excited electronic states, of molecules containing 4f and 5f elements. These magnetic properties can also be measured in the laboratory. Once we have established their relation to structure & bonding for well-characterized compounds it will be possible to characterize other compounds via measurements of their magnetic properties. We develop and apply state-of-the-art relativistic theoretical methods, for example for computing of magnetic resonance parameters (electron paramagnetic resonance = EPR, nuclear magnetic resonance = NMR) and magnetic susceptibilities of lanthanide and actinide complexes, and perform benchmark studies in comparison with well-characterized transition metal complexes. The project goals include developments of new relativistic quantum chemical methods in the open-source NWChem quantum chemistry package and other quantum chemistry programs, and the development of chemically intuitive analysis methods for the calculated molecular properties.

FY 2014 HIGHLIGHTS

Highlights of the 2014 fiscal year include several theoretical studies of a variety of uranium(V), uranium(IV), neptunium(VI), and plutonium(VI) compounds with unpaired electrons. Calculated magnetic properties were in good agreement with experimental data available in the literature. New methods were used in these studies allowing a description of chemical bonding and the distribution of the unpaired electrons and their magnetization in chemically intuitive terms. Further, connections of current state-of-the-art calculations with older much more approximate theoretical methods (chiefly: crystal field theory) were established. A new method to calculate hyperfine coupling constants for ligand atoms in f-element complexes within a multi-reference quantum chemical framework was developed and tested. These hyperfine constants probe the shape and spatial distribution of unpaired electron spins from the actinide or lanthanide f-shells. Going forward, this will allow us to interpret complicated nuclear magnetic resonance spectra of actinide complexes. A book chapter was written jointly with other developers of the NWChem program, highlighting its capabilities for predictive modeling of complex actinide systems. These capabilities include relativistic density functional methods for magnetic properties developed by us during previous budget periods.

Synthetic, Spectroscopic, and Computational Studies of Redox-Active Uranium Complexes for Fundamental Organometallic Reactions

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Funding: \$150,000 (2014)

PROGRAM SCOPE

The principal investigator's laboratory is studying the synthesis, characterization, and reactivity of reduced uranium complexes. We propose the study of two redox active ONO ligands, 9-hydroxyphenoxazin-1-one (ONOphen), which consists of a 3 ring framework, and the bisphenol amine, (ONOcat), which is composed of two phenolic rings linked by an amine. These ligands can be easily tuned sterically and electronically by using substituted phenols, and formation of strong uranium-oxygen bonds make this class of ligands an excellent candidate for supporting low-valent uranium centers. These ligands can accept two electrons into the energetically low-lying π^* orbitals, allowing them to shift between monoanionic or trianionic supporters. Our studies will focus on several themes: 1) the synthesis of low-valent uranium derivatives supported by these redox-active ligands, 2) reactivity of these species for organometallic reactions and catalytic applications, and 3) spectroscopic, magnetic, and computational studies. This is a multi-disciplinary study that will examine the electronic structure and bonding environment of uranium complexes capable of performing multi-electron chemistry. Our proposed studies contribute to the general fields of actinide chemistry and organometallics by expanding the understanding of the chemical potential and unique properties of uranium, as we plan to combine both synthetic and spectroscopic techniques to develop uranium species that perform reactions necessary for catalysis applications. Using redox-active ligands to store and transfer electrons in multi-electron steps has been rarely studied with uranium, thus our studies will provide valuable insight into the fundamental reactivity of uranium. Finally, using uranium to produce useful materials that have an impact on daily lives will help to promote the message that uranium is not just for destruction, but can be used for consumer products and as a valuable carbon neutral fuel.

FY 2014 HIGHLIGHTS

We are currently exploring a family of redox-active ONO ligands, [ONOcat] and [ONOphen] ([ONOcat] H_3 = N,N-bis(phenol)amine); [ONOphen] H_3 = 9-hydroxyphenoxazin-1-one), for their ability to support uranium in varying oxidation states. Both the ligands have been successfully synthesized and metallated, and derivatives are currently being fully characterized. Their organometallic derivatives, Cp*U(ONOcat) and Cp*U(ONOphen), which have transonic ligands supporting tetravalent uranium centers, have also been synthesized and characterized by X-ray crystallography. These studies have recently been submitted to the journal *Inorganic Chemistry*. We also began exploring pyridine(diimine) ligands as an alternative to the ONOphen system, due to the difficulty in synthesizing this class of ligands. A series of pyridine(diimine) uranium compounds were synthesized by sequential reductions with potassium graphite, generating highly reduced uranium coordination complexes with ligands storing one, two, three, or four electrons. Full characterization of these molecules, including collaborative work with Prof. Laura Gagliardi, Dr. Stosh Kozimor, and Prof. Eric Schelter, has recently been submitted to the *Journal of the American Chemical Society*. These species easily reduce organic azides, forming uranium mono-, bis-

, and unprecedented tris(imido) products. The latter class of compounds are unprecedented for actinide species, demonstrating that oxidation of uranium species bearing reduced redox-active ligands is an effective route to previously unobserved moieties. All reported species have been spectroscopically and structurally characterized in our laboratory, and additional studies have been performed by Prof. Gagliardi, Prof. Schelter, and Prof. Justin Walensky. This work has recently been published in Nature Chemistry.

Actinide Sorption and Reduction on Sulfides, Oxides and Clay Minerals

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Funding: \$100,000 (2014)

PROGRAM SCOPE

In five publications, the mechanism of uranium reductions on semiconducting sulfide and oxide mineral surfaces is investigated. These studies reveal that typically, U(VI) is first reduced to U(V) before being further reduced to U(IV) or disproportionated to U(IV) and U(VI). In addition, it was found under which conditions U(V) or U(V)-containing solids form at least metastable states. In these sub-projects, significant progress has been made in method-development of the powder microelectrode, the single-crystal mineral electrode, and in the use of electrochemical atomic force microscopy to study redox reaction mechanisms on mineral surfaces. Electrochemical AFM allows one to observe *in situ* the growth of reduced U adsorbates on mineral surfaces as a function of solution pH, chemistry, and set electrochemical potential. In addition, samples were analyzed using EXAFS and XANES and, as a spinoff, an *in situ* electrochemical reaction cell was developed that allows for real-time structural and oxidation states changes using x-ray absorption spectroscopy. Both techniques are now available for powder and single-crystal applications. In addition, eight more publications have resulted from this grant on the atomic and electronic structure of actinide-containing metal organic frameworks, the thermodynamics of actinyl incorporation into carbonate, sulfate, and oxide minerals, as well as uranyl alteration phases, the thermodynamics of the UO₂-HfO₂ solid solution to evaluate the role of burnable poisons on nuclear fuel performance, and the mechanism and rate of He diffusion as a result of α -radiation from U in minerals.

FY 2014 HIGHLIGHTS

To understand the atomistic mechanism and kinetics of actinyl redox processes, quantum-mechanical electron transfer calculations involving Marcus theory have been performed. Electron-transfer (ET) calculations on the first rate-limiting ET-step (the reduction of U(VI)aq to U(V)aq by Fe(II)aq) complement the experimental results. The homogeneous reduction of U(VI)aq to U(V)aq by Fe(II)aq is thermodynamically and kinetically favorable if an inner-sphere complex can be achieved. However, significant thermodynamic and kinetic barriers exist to proceed from an outer-sphere ET reaction to an inner-sphere ET reaction, a process that needs to overcome dehydration of the first solvation shell and hydrolysis of Fe(II)aq. One publication from this grant reviews, evaluates, and expands the theory behind the calculation of redox potentials in solution for species such as organic compounds, inorganic complexes, actinides, battery materials, and mineral surface-bound-species. Different computational

approaches to predict and determine redox potentials of electron transitions are discussed along with their respective pros and cons for the prediction of redox potentials. This article reviews the importance of computational parameters, such as basis sets, density functional theory (DFT) functionals, and relativistic approaches and the role that physicochemical processes play on the shift of redox potentials, such as hydration or spin orbit coupling. In a new line of research, we evaluate the thermodynamic, structural, electronic, optical, and catalytic properties of actinide-containing metal organic frameworks (An-MOFs) which may be used for the determination of the potential of An-MOFs for photo-enhanced catalytic processes. Metal organic frameworks (MOFs) are a relatively new class of hybrid crystalline materials composed of metal ions or metal-clusters and organic molecules as building blocks.

EARLY CAREER: Actinide N-Donor Thermodynamics: Expanding the f-element Covalency Dialogue

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Funding: \$750,000 (2014-2018)

PROGRAM SCOPE

Unraveling the fundamental chemistry of the heaviest elements remains a grand challenge of science. Challenges associated with studying the heaviest elements stem from their radiological hazards and lack of availability. Understanding this chemistry will only become more important as nations worldwide consider and develop peaceful nuclear technology to meet future energy demands. To address current knowledge gaps, this research will study the chemistry of the actinide elements uranium, neptunium, plutonium, americium, curium, berkelium, californium and einsteinium. While most of the elements to be studied have reasonable availability, the berkelium and einsteinium isotopes will be produced using U.S. Geological Survey's TRIGA[®] Reactor. The thermodynamics of the interactions of these elements with nitrogen donor complexants (nitrogen complexants that donate electrons) will be investigated to gain insight into how these elements share electrons with other elements or materials. The interaction of actinides with these complexants is particularly interesting as nitrogen has demonstrated some ability to share electrons (bind covalently) with actinides. Resolving this chemistry will allow for improved management of used nuclear fuel and provide the United States with key fundamental knowledge in this important area of technology. The data that will be gathered at the extreme edge of the periodic table will elucidate uncertain and suspected periodic trends.

FY 2014 HIGHLIGHTS

FY 2014 Highlights: I started receiving project funding September 1, 2014. During this time, I was able to hire a postdoctoral researcher for the project, recruit a graduate student and initiate a literature review for publication in FY15. The graduate student is currently being sponsored in a teaching assistantschips. Efforts were initiated in evaluating the thermodynamic data for americium complexation by acetate.

Topological Structural Relationships, Properties, and Nano-Structures of U(VI), Np(V), Pu(V) and Pu(IV) Materials

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Funding: \$140,000 (2014)

PROGRAM SCOPE

The structural chemistry of the actinides is extremely varied, complex and fascinating. Recent studies have clearly indicated that actinide structural chemistry, especially as it pertains to transuranic elements, is an underdeveloped field. Many important actinide materials await discovery that will provide novel insights into actinide solid state chemistry. The revolution in the understanding of the crystal chemistry of U(VI) that has occurred over the past dozen years provides the foundation for extension of such studies into the transuranic elements, especially Np(V). Ultimately, a detailed understanding of the structural chemistry of Np(V) that approaches the current state of knowledge for U(VI) will be achieved. The specific objectives of this program are as follows. (1) Continue to synthesize and determine the structures of a chemically diverse suite of Np(V) compounds, develop topological relationships within this group of structures and those of U(VI), and study the magnetic properties of well-characterized Np(V) compounds. (2) Synthesize and characterize a broad range of compounds containing highly unusual U(VI) cation-cation interactions, and delineate the conditions under which such interactions are favored, to understand the impact of U(VI) cation-cation interactions on structural stability. (3) Renew efforts to crystallize Th nano-scale clusters (polymers), guided by small-angle x-ray scattering studies of mother solutions and studies of the crystal-chemistry of Th. (4) Train two Ph.D. graduate students and one post-doc in solid state actinide chemistry. Through research assistantships and supervision, introduce six undergraduate students, over three years, to actinide research.

FY 2014 HIGHLIGHTS

We have made progress in answering longstanding questions about the origin of uranyl peroxide complexes following the sunlight photolysis of uranyl nitrate and uranyl acetate solutions in pyridine, demonstrating that they arise from photochemical oxidation of water.¹ We developed methods for ionothermal synthesis of novel uranyl compounds, and examined relationships between their structural units and interstitial complexes. The exclusion of water provides insights relative to typical uranyl minerals and compounds synthesized using the more common hydrothermal approach.²⁻⁴ Studies of cation-cation interactions in actinide solids resulted in the several novel examples.^{5,6} We synthesized and characterized uranyl diphosphonate and arsonate compounds with new structure topologies, including nanotubular and nanocage arrangements of building units.⁷⁻⁹ Studies revealed complex uranyl-based structure topologies.^{10,11}

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Novel Uranyl Bearing Materials via Restricted $\text{UO}_2^{\text{n}+}$ Speciation Profiles and Supramolecular Assembly

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 Sr. Investigator(s):
 Students: 0 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
 Funding: \$105,000 (2014)

PROGRAM SCOPE

The uranyl ion is subject to hydrolysis in aqueous media, which in turn leads to a diverse speciation profile that complicates the assembly of extended crystalline networks. As such, we have explored synthesis strategies in low pH, high-halide or high thiocyanate containing media to produce restricted speciation profiles. For thiocyanate media, the $[\text{UO}_2(\text{NCS})_4(\text{H}_2\text{O})]^{2-}$ tecton forms almost exclusively and thus provides a reproducible building unit for assembly with various organic cations such as substituted pyridinium cations (4-XpyH (where X = CH_3 , NH_2 , $\text{N}(\text{CH}_3)_2$, Cl, Br, I, SCN) Moreover, cations that are capable of sustaining multiple non-covalent interactions have been explored to provide a platform for multiple assembly modes. This strategy has led to the synthesis novel families of compounds and has provided a forum for systematic study of the predominant supramolecular interactions (i.e. halogen and hydrogen bonding) with respect to acceptor donor pairing. As a consequence, we are able to explore and rank and relative strengths of such interactions.

FY 2014 HIGHLIGHTS

A relative scale of interaction strengths responsible for the self-assembly of the uranyl isothiocyanate tecton and pyridinium molecules was published in *CrystEngComm* (December 2013; <http://dx.doi.org/10.1039/c3ce42106f>) and featured as a cover article and as a 'Hot' article on the Royal Society of Chemistry Blog: <http://blogs.rsc.org/ce/category/hot-article/>

Origin of Actinide Ion Partitioning in Biphasic Systems

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 Sr. Investigator(s):
 Students: 1 Postdoctoral Fellow(s), 1 Graduate(s), 1 Undergraduate(s)
 Funding: \$160,000 (2014)

PROGRAM SCOPE

Liquid-liquid solvent extraction for the isolation of metals is an essential feature of many processes within the nuclear fuel cycle. It is used in mining of uranium ore, fuel manufacturing, fuel recycling and reprocessing, and in waste treatment and management. The success of extraction derives from solute-solvent interactions, aqueous complexation and complex-adduct formation, as well as long-range properties described by the activity factors of the solutes in the pure phases. Empirical theories that describe solvent extraction are known, however advances in computational methods provide impetus for new models that incorporate a fundamental understanding of the underlying multi-scale physical phenomena. For extraction processes to become economically feasible and to design new separations approaches for the next generation of nuclear reactors, we must go beyond empirical observations and understand the fundamental molecular forces and mechanisms that govern metal speciation, complexation, and transport across phase boundaries. The scope of the project is to utilize multiscale theoretical methods and novel data analyses to characterize model Purex raffinate solutions and extraction systems, where deviations from solution ideality and changes in actinide hydrophobicity form the fundamental driving forces for successful extraction. This will provide an improved understanding of how perturbations to the H-bonding network and dynamics of water influence actinide complexation reactions and transport across aqueous:organic phase boundaries. The project uses simultaneous density functional theory calculations and molecular dynamics simulations that provide electronic structure and ensemble correlations of molecular systems. Novel data analysis provides the key to achieving insight into the structural and dynamic effects that are imparted by high ion concentrations and the hydrophobic character of extracting ligands and of neutral metal-ligand complexes.

FY 2014 HIGHLIGHTS

Major progress has been made in 3 core research areas:

- 1) Decomposing Hydrogen Bond Dynamics into Multiscale Components for the Development of a Hydrophobic Scale. Two manuscripts were published that outline a new software program that can quantify at a very high level of detail the dynamics of hydrogen bonding in a wide variety of chemical environment. A new algorithm was developed that allowed for more accurate calculation of hydrogen bond lifetimes so that all analyses can be better correlated with ultra-fast experimental studies.
- 2) Quantification of Organization and Dynamics at Aqueous:Organic Interfaces - Understanding How Mesoscale Interfacial Properties are Related to Miscibility and Microsolvation Reactions. One manuscript was published and another submitted that examined a special class of chemical reactions that occur at oil:water phase boundaries, microsolvation reactions. Microsolvation is defined as the rare event where one solvent molecule temporarily penetrates the co-solvent phases and is fully solvated therein. These reactions are the underlying processes that lead to permeability of an interface and are, we believe, correlated to rates of transfer of solutes across an interface. Our research examined the how microsolvation reactions are altered by the shape and packing ability of the organic solvent, and also the presence of an amphiphilic solute.
- 3) Accurate Solution Phase Thermochemistry of Actinides Across Oxidation States. In a published manuscript we developed a new computational protocol for obtaining highly accurate solution phase thermodynamic values for actinides in solution phase conditions that mimic Purex raffinates. Of specific importance in this context is to have equally accurate values for a wide variety of oxidation states of the actinide ions such that thermodynamic properties can be compared on equal footing for different chemical reactions.

Expanding the Fundamental Chemistry of Actinide Complexes

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Funding: \$430,000 (2013-2014)

PROGRAM SCOPE

The objective of this research is to expand actinide chemistry to provide information that may be useful in the development of advanced nuclear fuel cycles. This research also provides training of graduate students who will be the next generation of scientists skilled in the chemistry of the f orbital metals, the lanthanides and actinides. This project involves examination of areas of uranium and thorium chemistry that have high potential to broaden heavy element chemistry. One of the fundamental aspects of any metal, the range of accessible oxidation states, is being studied to look for new actinide metal oxidation states. Underdeveloped reaction types, such as gas/solid reactions and radical reactions, are being examined to expand their scope and applicability with actinides.

FY 2014 HIGHLIGHTS

The first crystallographically characterized example of a molecular complex containing uranium in the +2 formal oxidation state was prepared. The isolation and structural characterization of the tris(trimethylsilylcyclopentadienyl)uranium anion provides the first opportunity to examine the reaction chemistry of the +2 oxidation state of uranium. The complex is unusual in that the electron configuration appears to contain d orbital as well as f orbital components. Efforts to develop new options for reaction protocols for complexes of the actinide metals have led to the discovery that solid samples of organoactinide complexes will react with gaseous reagents at room temperature in the absence of solvent. Organoactinide reactions are traditionally conducted in solution since the starting materials are soluble and high temperatures used in solid-state reactions can be avoided. Now it is possible to accomplish hydrogenations using gaseous hydrogen and solid organouranium alkyl complexes to make organouranium hydride complexes in better yield than the solution hydrogenolyses reported over 30 years ago. Carbon dioxide is also a viable gaseous reactant with solid organoactinides. The radical reactivity of thorium metallocenes has been studied to get information about actinide radical reactions in well-defined molecular complexes. The reactions of actinide complexes with radicals are of general interest since nuclear waste stream remediation chemistry involves radiolytically generated radicals. Reactions of thorium metallocenes with 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) have revealed that TEMPO can bind to thorium as a neutral radical, can replace anionic ligands such as methyl, hydride, and bromide, and can replace polydentate pentamethylcyclopentadienyl ligands. The radical reactions are synthetically useful to change actinide coordination environments since reproducible reactions are observed with high yields in most cases.

Multiconfigurational Quantum Chemical Study of Actinides and Lanthanides Containing Systems

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Sr. Investigator(s):

Students: 1 Postdoctoral Fellow(s), 2 Graduate(s), 1 Undergraduate(s)

Funding: \$177,000 (2014)

PROGRAM SCOPE

We will develop and employ quantum chemical models in order to study the chemistry of systems containing actinides and lanthanides in the gas phase, in low temperature matrices, and in condensed phase. The proposed research involves a strong collaboration with several of the experimental groups funded within the BES Heavy Elements Program. More specifically we intend to address the following problems:

1) Structural and spectroscopic characterization of molecules containing actinides and lanthanides in the gas phase and matrices

We will study actinide carbide cluster cations of compositions $[An_mC_n]^+$, with $m = 1$, $n = 2-14$, and $m = 2$, $n = 2-18$. These species have recently been produced by laser desorption/ionization or laser ablation coupled with mass spectrometry in the laboratories of Dr. John Gibson and Dr. Lester Andrews. The structures of the larger species are uncertain and theoretical studies are of importance.

2) Reactivity and spectroscopy of inorganic and organometallic compounds containing actinides

Besides isolated species in the gas phase, we are interested in studying systems in a condensed phase that may be relevant for catalytic purposes in inorganic, organoactinide chemistry, or for the design of new materials. We will investigate oxidative addition and reductive elimination reactions with f elements. Actinides do not have the two-electron redox couples that facilitate such reactions, as occurs in transition metal chemistry.

3) The ground and excited states of actinide and lanthanide ions in solution

We will also investigate actinide chemistry in solution, which is related to the separation, transport in the environment and safety of nuclear waste disposal. We will study the capture of uranyl, by a recently engineered protein (Zhou *et al.* Nat. Chem. 2014, 6, 236) with high selectivity and femtomolar sensitivity and predict new proteins with even enhanced selectivity for uranyl.

FY 2014 HIGHLIGHTS

- 1) In collaboration with Paula Diaconescu we studied the electronic structure of the arene-bridged complex in relation to a variety of mononuclear uranium amide complexes. The syntheses, molecular, and corresponding spectroscopic and magnetic properties were measured and interpreted with reference to results of DFT and CASPT2 calculations performed on model compounds.
- 2) We characterized the electronic structure of several actinide-containing molecules recently measured by various experimental groups. In collaboration with John Gibson we investigated gas-phase molecular thorium and uranium carbide cluster cations of composition $An_mC_n^+$, with $m = 1$, $n = 2-14$, and $m = 2$, $n = 3-18$. DFT computations were performed to illuminate this distinction between the thorium and uranium species.
- 3) In collaboration with Suzanne Bart we showed that a redox-flexible pyridine(diimine) ligand can stabilize a series of highly reduced uranium coordination complexes by storing one, two or three electrons in the ligand. These species reduce organoazides easily to form uranium–nitrogen multiple bonds with the release of dinitrogen. Computational analyses of the uranium imido products probed their molecular and electronic structures, which facilitated a comparison between the bonding in the tris(imido) structure and its tris(oxo) analogue.

- 4) We studied the capture of uranyl, by a recently engineered protein with high selectivity and femtomolar sensitivity. We found that UO_2^{2+} is coordinated to five carboxylate oxygen atoms from four amino acid residues of the super uranyl binding protein (SUP). A network of hydrogen bonds between the amino acid residues coordinated to UO_2^{2+} and residues in its second coordination sphere also affects the protein's uranyl binding affinity. The results of our free-energy simulations confirmed the previously reported experimental results and allowed us to discover a mutant of SUP.

Exploring the Reactivity of the Uranyl Ion and Its Chalcogen Analogues: Expanding Our Understanding of Uranyl Reactivity and Behavior

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Funding: \$150,000 (2014)

PROGRAM SCOPE

In both the environment and in processed nuclear fuel uranium exists primarily as the uranyl ion (UO_2^{2+}). Understanding its bonding and reactivity is critical for understanding uranyl speciation, predicting redox behavior, and developing a proliferation-resistant fuel cycle that minimizes waste and consumes the transuranic elements found in spent fuel. To help achieve these requirements, the first goal of this project is to expand the oxo ligand functionalization chemistry of uranyl, and understand its influence on the reduction of the 6+ oxidation state to the 5+ and 4+ states. Improved understanding of the electronic interactions and structural properties that facilitate oxo functionalization will enable the design of better methodologies for actinide decontamination. To achieve this goal we will: (1) Study the reactions of electron-rich uranyl complexes with a variety of hydride sources, such as silanes (R_3SiH). (2) Develop Lewis acids capable of effecting the catalytic reduction of uranyl to UO_2 at ambient temperatures and pressures. These studies could have industrial significance, with potential applications in the processing of nuclear fuel. The second goal of this project is to synthesize and study new uranyl analogues, specifically the chalcogen analogues of uranyl, $[\text{E}=\text{U}=\text{E}]^{2+}$ ($\text{E} = \text{S}, \text{Se}, \text{Te}$). By synthesizing and characterizing new derivatives of uranyl we expect to achieve a greater understanding of its complicated electronic structure. Understanding this bonding picture is necessary for firming predictions of uranyl behavior in both the environment and in spent fuel. Additionally, we anticipate the discovery of new modes of reactivity, with potential applications to organic synthesis and small molecule activation. To achieve this goal we will: (1) Explore the synthesis and reactivity of new terminal uranium chalcogenide complexes. (2) Develop new chalcogen transfer reagents and apply these to the synthesis of the chalcogen analogues of uranyl.

FY 2014 HIGHLIGHTS

We recently reported the ability of KSCPh_3 to act as a convenient sulfur atom source. In particular, reaction of KSCPh_3 with $[\text{U}(\text{NR}_2)_3]$ resulted in formation of a terminal sulfide, $[\text{K}(18\text{-crown-6})][\text{U}(\text{S})(\text{NR}_2)_3]$ ($\text{R} = \text{SiMe}_3$), via spontaneous release of the trityl radical. No doubt, this mode of reactivity is enabled by the low C-S bond dissociation enthalpy in $[\text{SCPh}_3]$. The trityl elimination strategy can also be applied to the synthesis of a terminal oxo complex. Specifically, reduction of $[\text{U}(\text{OCPH}_3)(\text{NR}_2)_3]$ with 2 equiv of KC_8 ,

in the presence of 18-crown-6, results in the formation of $[K(18\text{-crown-6})][U(O)(NR_2)_3]$ and $[K(18\text{-crown-6})(THF)_2][Ph_3C]$, which were isolated in 36% and 52% yield, respectively. To our knowledge, this is the first example of reductive deprotection of trityl to form an oxo ligand, and demonstrates that traditional organic deprotection protocols can be applied to inorganic synthesis. Importantly, this work also demonstrates that the trityl group can be cleaved from the heteroatom by two different mechanisms: either spontaneous loss of trityl radical or reductive cleavage of the trityl group or loss of the trityl anion.

Selective Recognition of Heavy Element by Protein Based Reagents

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Funding: \$209,000 (2014)

PROGRAM SCOPE

The objective of this project is to engineer protein-based reagents that can selectively bind heavy elements in aqueous solutions. In fiscal year 2014, our work on the development of a uranyl-selective binding protein that binds uranyl with high affinity and selectivity was completed and published. Through collaboration with Professor Laura Gagliardi, we further improved the current uranyl-binding protein based on computational analysis. This result was just accepted for publication. We are in the process of setting up a potential high-throughput screen strategy that would enable us to perform direct evolution in order to select proteins that may bind uranyl with even higher affinity. During our initial research on uranyl-binding proteins, a program called URATEIN was created to search for possible uranyl-binding sites in protein scaffolds. We initiated a new research direction by modifying this program to search for proteins that may contain the necessary octo-coordination sites to chelate lanthanide and actinide ions. Over a hundred different proteins were identified after searching through more than 34,000 PDB entries, and of these six were identified through manual selection for expression based on structure and anticipated ease of expression. All genes were subcloned into pet28a for expression in the BL21 strain of *E. coli*. We are developing binding assays and testing binding affinities of these selected candidates.

FY 2014 HIGHLIGHTS

Uranyl is present in the ocean at a concentration of ~ 13.7 nM. We have engineered a thermally stable protein that binds uranyl tightly (K_d of 7.4 femtomolar) and highly selectively ($>10,000$ -fold selective over other metal ions). This protein can repeatedly sequester 30-60% of the uranyl in synthetic sea water. This system could find broad applications in uranyl sequestration, bioremediation, and other biotechnology applications.

Zhou, L.; Bosscher, M.; Zhang, C.; Ozcubukcu, S.; Zhang, L.; Zhang, W.; Li, C. J.; Jensen, M.; Lai, L.; He, C. *Nat. Chem.* 6, 236 (2014).

Spectroscopic Studies of Prototypical Actinide Compounds

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Funding: \$145,000 (2014)

PROGRAM SCOPE

This program investigates actinide bonding mechanisms and electronic structure via high-resolution electronic spectroscopy. To obtain data that are best suited for evaluation of theoretical models, small actinide-containing molecules (di- and tri-atomic) are studied in the gas phase. Laser excitation and dispersed fluorescence techniques are used to characterize the neutral molecules, while sequential two-photon excitation measurements are used to determine ionization energies and physical properties of molecular ions. High level theoretical calculations are carried out for comparison with the experimental results, in order to evaluate the predictive capabilities of current relativistic quantum chemistry models. Our most recent experiments have focused on the molecules ThN/ThN⁺, ThS/ThS⁺, ThF/ThF⁺, and UF/UF⁺

FY 2014 HIGHLIGHTS

The electronic spectrum of ThN, which is isoelectronic with ThO⁺, was recorded for the first time. Rotationally resolved spectra confirmed the ground state to be X²Σ⁺, derived from the Th(7s)N configuration. The characteristics of ground state ThN, including the spin-rotation constant, were found to be closely similar to those of HfN. Twenty vibronic bands of ThN were characterized in the 19800-21200 cm⁻¹ energy range. The ionization energy of ThN (6.3272(4) eV) and the molecular constants for ThN⁺ were determined using two-color photoionization. The ground state symmetry was found to be X¹Σ⁺, as expected for ionization by removal of the Th 7s electron. Relativistic quantum chemistry calculations yielded predictions that were in reasonably good agreement with the experimental results for both ThN and ThN⁺. High resolution Stark spectroscopy was used to measure the permanent dipole moment of ThS X¹Σ⁺ (collaboration with T. Steimle, Arizona State University). The value obtained, 4.58(10) D was used to evaluate the quality of single-reference and multi-reference quantum chemistry calculations. Despite indications that ThS should be treated using multi-reference techniques, it was found that the single-reference methods were successful if the reference determinant was suitably chosen. The preliminary indication from this study is that computationally inexpensive Density Functional Theory methods can be used to obtain reasonably good predictions for open-shell actinide species. New laser excitation spectra for the ThF⁺ ion were recorded to determine the symmetry of the ground state. Rotationally resolved data for a transition centered at 20506 cm⁻¹ were used to definitively identify the ground state as X¹Σ⁺. With a low-lying 3Δ1 state, this molecule is ideal for measurement of the electric dipole moment of the electron (eEDM). To facilitate the design of eEDM experiments we used high-level quantum chemistry calculations to predict the low-lying electronic states.

Accurate *Ab Initio* Thermochemistry and Spectroscopy of Molecules Containing f-block Elements

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Principal Investigator: Kirk Peterson

Sr. Investigator(s):
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Funding: \$125,000 (2014)

PROGRAM SCOPE

The primary goal of the present program is to develop and then implement the *ab initio* methodology required for chemically accurate thermochemical and spectroscopic investigations of atoms and molecules containing heavy elements, with particular emphasis on lanthanides and actinides. The accuracy goal for thermochemical quantities, e.g., bond dissociation energies, heats of formation, electron affinities, etc., is 1-3 kcal/mol. These studies are based on extensions to the Feller-Peterson-Dixon composite approach, which hinges on recovering all important contributions to thermochemical quantities as accurately as possible. Highly correlated wavefunction-based approaches are employed, like coupled cluster singles and doubles with perturbative triples, CCSD(T), or multireference configuration interaction (MRCI) and perturbation theory (CASPT2), with a series of correlation consistent basis sets that allow for reliable extrapolations to the complete basis set (CBS) limit. This methodology will then be applied to fundamental, gas phase actinide- and lanthanide-containing species to assist existing, as well as future, experimental studies.

FY 2014 HIGHLIGHTS

Two series of correlation consistent basis sets, one based on small-core energy consistent pseudopotentials and the other using the all-electron, 3rd-order Douglas-Kroll-Hess Hamiltonian, have been developed for both Th and U from double- through quadruple-zeta, including sets for recovering 5s5p5d correlation effects. These sets have been used in extrapolated CBS limit coupled cluster thermochemistry studies of ThF_n (n=2-4), ThO₂, UF_n (n=4-6), UO₂F₂, UO₃, and UO₂(OH)₂ that included contributions due to core correlation, spin-orbit coupling, and lamb shift effects. The all-electron approach yielded heats of formation that agreed to within the experimental uncertainties in nearly all cases (UO₃ was the slight exception) with some results predicted to be more accurate than the existing experimental values (e.g., UO₂(OH)₂). The pseudopotential approach became less accurate when the process involved a large change in oxidation state of the actinide.

Experimental Electron Density Distribution in Actinide Compounds - An Experimental Atoms in Molecules Approach

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Funding: \$500,000 (2014-2016)

PROGRAM SCOPE

Chemical and most physical properties of materials are dependent on the distribution of the valence electrons. This distribution is easily measurable for crystalline light atom containing materials using the tools of X-ray diffraction, but until recently was an intractable problem for compounds of heavy elements. Recent developments in hardware and software for X-ray diffraction in our laboratory allow

more ambitious experiments to be proposed than previously. We thus address a fundamental question in the chemistry of the actinides – the nature of the actinide-ligand bond, particularly with respect to the degree of covalence. We are now able to measure the valence electron density distribution in compounds of elements as heavy as thorium or uranium using the technique of cryo-crystallography, followed by the fitting of a multipole model of the electron density to the X-ray diffraction data. The systems proposed for study are selected compounds of Th^{4+} , U^{4+} and of the uranyl ion. We will determine the electron density distribution and its topology in order to examine the characteristics of the strong uranyl $\text{U} \equiv \text{O}$ bond, as well as the weaker bonds between the actinide metals and other ligands of varying hardness. This challenging project will provide significant insight into the chemical bonds to actinide ions, as well as provide benchmark data to evaluate different theoretical methods. Given the current resurgence of interest in nuclear power generation, nuclear fuel processing, and the concern for the environmental impact, we will provide needed new understanding of the basic chemistry of these elements.

FY 2014 HIGHLIGHTS

Funding for this proposal only became available on August 26, 2014, hence accomplishments are limited. A high resolution x-ray diffraction experiment at 20K has been carried out on sodium uranyl acetate. Analysis of the data is incomplete.

Accurate Theoretical Approaches for Studying Actinides and Other Heavy Elements in Solid State

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Funding: \$135,000 (2014)

PROGRAM SCOPE

Theoretically describing solids containing lanthanides or actinides is far from straightforward. This is because the f electrons can delocalize into a conduction band, form a chemical bond, or localize onto the lanthanide or actinide center. The potentially large number of localized electrons leads to a large number of potential magnetic structures. Methods which treat actinides or lanthanides must then be able to treat the various magnetic structures and the various possible behaviors of the f electrons on an equal footing. Actinide solids are crucial components of nuclear reactors. The actinide oxides focused on in this proposal are typical nuclear fuels; ideally, they would be replaced by actinide nitrides or carbides, which have superior refractory properties. Experimental characterization of actinide nitrides and carbides is fraught with difficulties, and theoretical investigations fare little better. This proposal seeks to continue the theoretical study of actinide oxides and to develop techniques capable of describing the actinide nitrides and carbides. Such theoretical investigations form an important counterpart for DOE-sponsored experimental research. This proposal seeks to develop sophisticated theoretical tools and apply them to the study of actinide materials. The theoretical techniques to be developed will fill an important void in the computational toolkit by combining low computational cost with an accurate description of strong correlations. The applications will enhance understanding of the magnetic behavior of actinide materials, as well as their behavior under extremes of pressure and temperature. In the long

term, they will provide a deeper understanding of actinide nitrides and carbides, which have the potential to be advanced nuclear fuels which will offer clean, carbon-neutral energy.

FY 2014 HIGHLIGHTS

These highlights correspond to the 2014 fiscal year. There were 5 publications acknowledging support from this grant during this period. Applications to actinide systems using density functional methods were carried out in collaboration with Xiadong Wen and Richard L. Martin from LANL. Applications to solid state actinide systems using the HSE functional developed in the PI's group are part of a long standing collaboration with Rich Martin's LANL research group. Methodological developments were carried out exclusively at Rice. Briefly, the most salient bullets have been: (1) A novel noncollinear density functional theory approach which is particularly important for heavy elements; (2) The implementation of full space symmetry group in our periodic boundary conditions code that will allow for much faster computations of crystalline solids; (3) The treatment of residual correlations not included by symmetry breaking and restoration (SB&R) techniques using a linearized Jastrow-type approach; (4) Development of a quantum embedding theory that will allow for accurate wavefunction calculations using Wannier functions on solids containing actinides; (5) Utilizing our SB&R wavefunction nodal surfaces in constrained-path quantum Monte Carlo calculations in collaboration with Zhiwei Zhang's group and partially supported by a CMCSN award.

Ion Pair Receptors: Fundamental Studies and Tests Involving Sulfate Anion and Thorium Cation Extraction

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Funding: \$495,000 (2014-2016)

PROGRAM SCOPE

As stated in the 2013 competitive renewal application, our goals during the current 3-year funding period are to continue our fundamental studies involving the development of ion pair receptors and their application to the recognition, sensing, and extraction of ions relevant to the DOE mission, including the uranyl (UO_2^{2+}), Th(IV), Cs^+ , and Li^+ cations, the chloride and sulfate anions, and various ion pairs derived therefrom. New work is designed to explore the possibilities of exploiting ion pair receptors as through-membrane transport agents with biomedical potential.

FY 2014 HIGHLIGHTS

We have made progress towards several of our stated project goals. Noteworthy was the synthesis of a new, bipyrrrole-strapped calixpyrrole receptor that was found to bind the sulfate anion and act as an effective extractant for this DOE mission-critical anion. This work was carried in conjunction with Dr. Bruce Moyer at Oak Ridge National Laboratory (ORNL) and members of his research team. Other work with strapped calixpyrroles led to the identification of the first systems wherein solid state self-assembly was promoted by ion pair recognition, as well as those wherein fluoride selectivity was engineered into the molecular structure. A particularly interesting finding made during the reporting period was the

discovery that one of our ion pair receptors, namely a pyridine diamide strapped calix[4]pyrrole, acted as an effective chloride transporter. As a consequence of this transport, apoptosis is induced in cancer cell lines. This work, which was carried out in conjunction with Profs. Philip A. Gale and Injae Shin, went “viral” on the internet after its publication in August of 2014 in Nature Chemistry. Apparently, the appeal to the broad, lay audience was the newly reported mode of action that basically involves the carrier-mediated transport of salt into cells. On the uranyl cation front, we completed our initial studies of cyclo[1]furan[1]pyridine[4]pyrrole (“F1P1P4”) and showed that this species not only complexed the uranyl cation well, but also assumed aromatic character as a result. A practical consequence of this change in electronic structure is that F1P1P4 acts as a highly effective sensor for the uranyl cation, with huge color changes being engendered as the result of cation complexation. To the extent the uranyl cation is a surrogate for the neptunyl and plutonyl cations, such a result may lead to improved detection protocols that could be applied in the event of untimely release of radioactive material.

Probing the Actinide-Ligand Binding and the Electronic Structure of Gaseous Actinide Molecules and Clusters Using Anion Photoelectron Spectroscopy

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Funding: \$270,000 (2014-2015)

PROGRAM SCOPE

This project focuses on the investigation of gaseous actinide-containing molecules using anion photoelectron spectroscopy. Three thrust areas are pursued: 1) probing the ligand-uranyl interactions in gaseous anionic complexes produced by electrospray ionization; 2) probing the electronic structure and chemical bonding of simple inorganic actinide compounds using electrospray and anion photoelectron spectroscopy; 3) probing the metal-metal bonding and size-dependent electronic structures in uranium oxide and fluoride clusters as a function of size and composition. Understanding the chemistry of the actinide elements, in particular, uranium, is of critical importance to the mission of DoE. The chemical properties of uranium are fundamental to the understanding of its speciation, transport, and eventual fate in the environment. Two state-of-the-art photoelectron spectroscopy apparatuses, one involving a laser vaporization cluster source and another involving an electrospray ionization source, are used in this project. Two new experimental capabilities, a temperature-controlled ion trap to create cold anions and a high resolution photoelectron imaging system, have also been developed and are used for this project. Photodetachment of anions involves removal of electrons from occupied molecular orbitals and probes directly the bonding properties of the underlying molecular species. Photoelectron spectroscopy of anions yields electron affinities, and low-lying electronic state and vibrational information for the corresponding neutral species. The application of anion photoelectron spectroscopy to actinide molecules has opened up new research opportunities and will yield a wealth of accurate and systematic electronic structure and spectroscopic information that can be used to verify computational methods and advance our understanding of the reactivity, structure, and bonding of actinide molecules.

FY 2014 HIGHLIGHTS

High Resolution Photoelectron Imaging of UO^- and UO_2^- and the Low-Lying Electronic States and Vibrational Frequencies of UO and UO_2 :

We have carried out a high resolution photoelectron imaging study to provide the electronic and vibrational information on two simple uranium oxide molecules: UO and UO_2 . The spectra for UO_2^- are consistent with, but much better resolved than our previous study using a magnetic-bottle photoelectron analyzer. The electron affinity (EA) of UO is obtained for the first time as 1.1407(7) eV, whereas a much more accurate EA is obtained for UO_2 as 1.1688(6) eV. The symmetric stretching modes for the neutral and anionic ground states, and two neutral excited states for UO_2 are observed, as well as the bending mode for the neutral ground state. The stretching vibrational modes for the ground state and one excited state are observed for UO . The current results for UO and UO_2 are compared with previous theoretical calculations including relativistic effects and spin-orbit coupling. The accurate experimental data reported here provide more stringent tests for future theoretical methods for actinide-containing species.

Observation of Gaseous UCl_6^- and UCl_6^{2-} Anions:

The Electronic Structures and Chemical Bonding of Uranium Hexachlorides We have produced two gaseous uranium chloride anions, UCl_6^- and UCl_6^{2-} and studied their electronic structure and chemical bonding using photoelectron spectroscopy and theoretical calculations. The EA of UCl_6 is measured for the first time as 5.3 eV and its second EA is measured to be 0.60 eV. We find that the one-electron molecular orbital picture and Koopmans' theorem break down for the strongly correlated U-5f2 valence shell of the tetravalent UCl_6^{2-} . Insight into the trend of the chemical bonding from $\text{U(VI)Cl}_6 \rightarrow \text{U(V)Cl}_6^- \rightarrow \text{U(IV)Cl}_6^{2-}$ is discussed.

DOE National Laboratories

EARLY CAREER: Harnessing f-Orbital Bonding through Precision Antenna Ligand Design for Actinide Complexation

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Funding: \$500,000 (2014)

PROGRAM SCOPE

The needs to resolve the role of f-electrons in actinide bonding and to understand and design new molecular systems that control the chemical selectivity of actinides constitute two scientific grand challenges in the development of improved materials and processes for nuclear applications. Controlling the selectivity of actinide-binding species in complex environments necessitates the ability to understand and predict fundamental coordination properties of actinide-specific ligands. The objective of this work is to enable selective tuning of spectroscopic and thermodynamic properties of specific actinide complexes through precision ligand design and molecular recognition. The actinide sensitization efficiency of selective chromophore-containing ligands through the antenna effect will be explored, to establish a library of functionalized ligands with specific actinide-binding properties and spectroscopic features. Systematic and iterative characterization of the designed species will be used to harness the

influence of f-orbital bonding on the differences in actinide complex energetic and coordination features, including kinetic, thermodynamic and optical properties. Understanding the fundamental bonding interactions of selective actinide ligands presents a rich set of scientific challenges and is critical to the development of highly efficient separation reagents. The approach taken in this project paves the way to fulfill this difficult task by combining the precision ligand design, sensitive luminescence characterization, and theoretical modeling. The information gained from this effort will not only provide molecular signatures for the designed actinide coordination systems, it will yield fundamental knowledge of the role of f-electrons in actinide bonding and spectroscopic properties and will lay the foundations for further spectroscopic and synthetic work and discovery related to nuclear energy applications such as separation and waste storage processes.

FY 2014 HIGHLIGHTS

This project was successfully started in the last quarter of FY2014, with significant progress in the spectroscopic and thermodynamic characterization of actinide species. The first americium luminescence sensitization experiments were carried out using established ligands containing several hydroxypyridinonate and catecholate metal-binding isomers: complex formation between Am(III) and the octa-, hexa-, and tetradentate ligands 3,4,3-LI(1,2-HOPO), enterobactin, and 5-LIO(Me-3,2-HOPO), respectively, was probed in aqueous solution. Upon excitation of all three ligand pi-pi* transitions, structured emission patterns were observed and attributed to the Am(III) transition 5D_0 to 7F_1 (with fluorescence quantum yields of the order of 0.01 %). A series of Am(III) sensitizers was therefore identified for the first time and will be used to build functionalized ligand platforms with tuned actinide sensitization properties. These luminescence properties were also used to determine complex formation constants, demonstrating higher stability for Am(III) complexes in comparison to the corresponding Eu(III) complexes, but lower stability than Cm(III) complexes. These data will be used for building empirical trends in bonding and coordination within the 5f element series, which will in turn be correlated with theoretical predictions. In addition, a new experimental setup for multi-photon absorption spectroscopy with radioactive actinide complexes was implemented, using a tunable laser as an excitation source. Both hydroxypyridinonate ligands mentioned above were found to act as two-photon probes for the sensitization of several trivalent lanthanide cations and of Cm(III). This is the first example and characterization of two-photon antenna sensitization of a transuranic actinide ion in solution, which paves the way for the detailed mapping of intermediate energy levels in 5f metal complexes.

Influence of Solution Phase and Interfacial Structure on Stability of Actinide Oxidation States: A Computational Approach

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Funding: \$49,000 (2014)

PROGRAM SCOPE

Knowledge of the oxidation states and reduction/oxidation (redox) chemistry of actinide elements in these complex environments, as well as the ability to predict, control, or manipulate them, is critical to

virtually all aspects of environmental actinide chemistry, waste processing, and separations. Comprehending the chemical behavior and properties of actinides as a function of structure and geometry of mineral/water interfaces at the molecular level is critical to a mechanistic understanding that can be propagated into field scale and of subsurface contaminant behavior and transport. With the availability of high-performance parallel computational resources and scalable software, computational chemistry can now be used to study the redox chemistry of actinides at experimentally relevant geochemical interfaces and in the presence of a mixture of interacting ligands in solution. This program focuses on the influence of dynamical local molecular environments on complex formation, redox mechanisms, preferred oxidation states, and the role of spin-orbit coupling, as well as the role of 5f electrons in the bonding of actinides in geochemically relevant solution environments and at complex solution/solid interfaces. We will use our highly scalable capabilities in Gaussian and plane-wave density functional theory (DFT), including the essential relativistic scalar and spin-orbit effects, and properly account for the influence of the local molecular environment.

FY 2014 HIGHLIGHTS

In FY14, *ab initio* molecular dynamics (AIMD) simulations were used to examine the hydration structures, coordination energetics, and the first hydrolysis constants of Pu^{3+} , Pu^{4+} , PuO_2^{2+} , and PuO_2^{2+} ions in aqueous solution at 300 K. The coordination numbers and structural properties of the first shell of these ions are in good agreement with available experimental estimates. The hexavalent PuO_2^{2+} species is coordinated to five aquo ligands while the pentavalent PuO^{2+} complex is coordinated to four aquo ligands. The Pu^{3+} and Pu^{4+} ions are both coordinated to eight water molecules. The first hydrolysis constants obtained for Pu^{3+} and PuO_2^{2+} are 6.65 and 5.70, respectively, all within 0.3 pH unit of the experimental values (6.90 and 5.50, respectively). The hydrolysis constant of Pu^{4+} , 0.17, disagrees with the value of -0.60 in the most recent update of the NEA Thermochemical Database but supports recent experimental findings. The hydrolysis constant of PuO^{2+} , 9.51, supports the experimental results of Bennett *et al.* [Radiochim. Acta 1992, 56, 15].

Since the project is being closed out we have made every effort in the last year to make our developments accessible to other actinide and lanthanide researchers. In FY14, we have completely re-implemented our localized basis projected augmented wave (PAW) AIMD codes so that they are faster, more parallel, and easier to use. This development is important for the far right lanthanides and actinides. These atoms have very stiff pseudopotentials, requiring very small AIMD time steps. As a result, simulations using our non-PAW AIMD codes take an order of magnitude longer to carry out than for other lanthanides and actinides. This important new development has less stiff pseudopotentials that makes AIMD simulations of systems containing the far right lanthanides assessable to actinide researchers (e.g., P. Yang (LANL), W. DeJong (LBNL), R. Atta-Fynn (UT Arlington)) and lanthanide researchers (H. Simka (Intel)).

NMR Spectroscopy of Plutonium Systems

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Funding:	\$638,000 (2014)

PROGRAM SCOPE

This project will evaluate magnetic resonance spectroscopy, ^{239}Pu nuclear magnetic resonance (NMR) especially, as a probe for Pu materials. By virtue of its place between the heavy actinides, whose electrons occupy atom-like states, and the light actinides, whose electrons delocalize into covalent or band-like states, plutonium is the pivotal element to investigate for insights into the extraordinarily rich electronic properties of the actinide series. Despite its potential for elucidating electronic structure and the favorable magnetic properties of the ^{239}Pu isotope, NMR spectroscopy has seldom been used for the study of Pu systems. With NMR instruments now available in radiological facilities at the Pacific Northwest National Laboratory (PNNL) and Los Alamos National Laboratory (LANL), and Pu samples of high quality at hand, we are in an unprecedented position to initiate NMR experiments of Pu-containing compounds of relevance to DOE missions. The primary objective is to measure ^{239}Pu and ^{17}O shielding and electric field gradient tensors and relaxation times in selected plutonium oxides. These parameters will enable us to visualize structures at defect sites and develop explanations for the complex behavior of nonstoichiometric PuO_2 . Recent work at LANL and PNNL suggests that the promise of ^{239}Pu NMR spectroscopy is within reach after 50 years of unsuccessful previous attempts. This multi-institution collaboration brings together the world's leading experts in the specialized procedures required for the synthesis and spectroscopic analysis of Pu materials.

FY 2014 HIGHLIGHTS

PuO₂ experiments. NMR spectra of PuO_2 have been collected in piecewise fashion over a 200,000 ppm range. Several resonances, probably originating from ^{239}Pu centers in a variety of crystalline and defect sites, have been observed, and are being investigated for assignments to putative microscopic environments.

Spectra of $(\text{Me}_4\text{N})_2\text{PuCl}_6$. An array of low temperature spectra has been acquired using the swept field NMR instrument at LANL. Like PuO_2 , $(\text{Me}_4\text{N})_2\text{PuCl}_6$ has a Pu(IV) center in a cubic environment, and is expected to have a singlet ground state that is favorable for ^{239}Pu NMR. A model assuming cubic symmetry, low magnetism, and small electric field gradients is being examined, and the interpretation of spectral features is in progress.

Theory development. In collaboration with Prof. Jochen Autschbach (University of Buffalo), who is a world leader in the computation of NMR parameters of heavy element systems, we seek to predict NMR parameters of Pu-containing systems. Knowledge of the shielding tensors of Pu and surrounding atoms is essential for the search of NMR lines and their interpretation in terms of the electronic environment. Also of interest is the energy and identity of the first excited state of cubic Pu^{4+} systems, which are critical to understanding the magnetic behavior of $5f^4$ systems.

Novel instrumentation and methods. Substantial effort has been devoted to management of the challenges of experimentation with Pu. Tubes and rotors designed by us are currently used to contain hazardous solid samples, but more recently we have pursued an alternative, superior approach that uses a sealed probe for radiological containment (Cho, *et al.*, U.S. patent pending). In addition, we have developed a process for making monolithic pellet-shaped samples that facilitate safe handling. Pellets made from PuO_2 synthesized by us have been created for current experiments. Technical Work Documents that codify our procedures have been prepared and approved.

An Integrated Basic Research Program for Advanced Nuclear Energy Separations Systems based on Ionic Liquids

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Funding: \$206,000 (2014)

PROGRAM SCOPE

Future advanced nuclear energy systems will require significant changes in the way nuclear fuel is processed, in order to achieve the increases in efficiency and reductions in waste sent to repositories that are necessary if nuclear power is to have a major role in serving the world's growing energy needs. Ionic liquids (ILs, salts that melt at low temperatures) enable technologies to achieve these goals. ILs have unusual physical properties and process safety advantages compared to ordinary solvents. Their properties can be controlled by design to fit a given need. This project explores the application of ionic liquids to nuclear separations processes with particular concern for their performance under ionizing radiation as found in separations conditions. A multidisciplinary team has been assembled to study the fundamental radiation chemistry of ionic liquids, learn how that chemistry interferes with separations efficiency in ILs, seek to prevent or mitigate such interference through substitution of ionic liquid components, and design and create ILs for more efficient and radiolytically robust separations chemistry. The goal is to replace current technologies with ones that allow more efficient use of resources and smaller environmental impacts, bringing us close to a sustainable energy future. The research effort at ORNL is a part of a project led by Dr. James Wishart at BNL that lies in development of ionic-liquid systems for separation of fission products.

FY 2014 HIGHLIGHTS

Solvent extraction of La^{3+} and Ba^{2+} by an ionic liquid extractant in an imidazolium-based ionic liquid diluent was investigated. Seven protic ionic liquid (PIL) extractants were examined based on five organic superbases and either 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octadione (Hfod) or 1,1,1,5,5,5-hexafluoroacetylacetone (Hhfac) β -diketones as the anion. For these PIL extractants, the extraction efficiencies and separation factors were found to be concentration dependent. Five new functionalized ionic liquids (FILs), tetraethylammonium di(2-ethylhexyl)phosphate, tetraethylammonium bis(2,4,4-trimethylpentyl)phosphinite, tetraethylammonium bis(2,4,4-trimethylpentyl)dithiophosphinite, tetrahexylammonium di(2-ethylhexyl)phosphate, and tetraoctylammonium di(2-ethylhexyl)phosphate were synthesized and characterized. These ILs along with two previously synthesized FILs were used as ionic extractants and investigated for rare earth elements (REEs) separation in $[\text{C}_{10}\text{mim}][\text{NTf}_2]/[\text{BETI}]$. These FILs as ionic extractants were miscible with $[\text{C}_{10}\text{mim}][\text{NTf}_2]/[\text{BETI}]$. A novel solvent extraction process for trivalent lanthanides and yttrium from aqueous solutions into ILs, which is promoted by a hydrophilic 1-methylimidazole (1-MIM) or 2-methylimidazole (2-MIM), was investigated. Slope analysis confirmed that MIM in ILs formed a 1:1 complex with La^{3+} and Y^{3+} and a 1:4 complex with Eu^{3+} and Lu^{3+} , depending on the atomic number of the metal. The metal–ligand interactions have been characterized by FTIR spectroscopy and ESI-MS. The effect of nitrate concentration on the extraction of lanthanides with 1-MIM in ILs was analyzed indicating that nitrate anions were involved in the extraction process.

EARLY CAREER: Molecular Transuranic Discovery Science: Underpinning National Energy Security and Waste Remediation Needs

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Funding: \$2,500,000 (2010-2014)

PROGRAM SCOPE

The aims of this research are to advance knowledge and understanding of transuranic coordination chemistry, electronic structure, and bonding (primary focus is upon the transuranic elements of plutonium and neptunium). The relevance of this project to DOE is to provide the basic chemical bonding information in support of development of novel actinide separation schemes for advanced nuclear fuel cycle processes and understanding how to control actinide speciation/behavior over a wide range of chemical environments. A central goal is to decipher the extent to which covalent bonding interactions are important in actinide complexes, the capacity of valence 5f and 6d orbitals to participate in metal-ligand interactions, differences between actinide and lanthanide bonding, and trends across the actinide series. There are two principal approaches to elucidating transuranic covalency in molecular systems that are under investigation. The first is to compare actinide/lanthanide bonding with 'soft' donor ligands, such as nitrogen, sulfur, and selenium, in which evidence for subtle covalency differences can be uncovered. The second is to isolate unprecedented transuranic metal-ligand multiple bonds that contain inherent covalent bonding character. Acquiring such detailed bonding understanding will ultimately facilitate rational molecular design processes for novel chemical solutions to nuclear fuel cycle and waste remediation challenges.

FY 2014 HIGHLIGHTS

New neutral An(IV) starting materials were developed, and published, to facilitate Np(IV) and Pu(IV) synthetic chemistry under anhydrous inert atmospheric conditions. Their preparations are high-yielding with X-ray single-crystal structural determinations performed. These tetrachloride-dimethoxyethane adducts have opened up access routes to previously unattainable target molecules. Of particular note, the Np(IV) starting material has been utilized in the isolation and solid-state structural determination of the first example of transuranic-ligand multiple bond that is not a dioxo cation. Specifically, a linear Np(V) bis-imido moiety was the product of reaction between the new Np(IV)-tetrachloride-dimethoxyethane adduct and an amide in the presence of bipyridine, a process during which Np(IV) is oxidized to Np(V), with the resultant product containing two Np=N bonds. The result demonstrates that the 5f and 6d orbitals are still accessible to engage in covalent multiple bonding interactions with 'soft' donors further across the actinide series than uranium, and also informs upon the redox stability of neptunium which is often problematic to control in processes. In a different system, a Np(IV) complex has been isolated and structurally characterized in which a tetradentate tris(amido) 'TREN' supporting scaffold has been installed onto the actinide metal center. This result now provides a platform to attempt to access a whole series of other metal-ligand multiple bonds, such as a terminal monoxo and chalcogenido groups, that can be used to develop covalency trends in comparison to uranium. In addition, characterization has been completed on a plutonium complex with a polydentate nitrogen

donor actinide selective extractant, in which it was demonstrated the Pu(IV) is unexpectedly reduced to Pu(III) upon complexation.

Heavy Element Chemistry

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Funding: \$1,286,000 (2014)

PROGRAM SCOPE

The central goal of the Los Alamos Heavy Element Chemistry program is to advance the understanding of unexpected covalency and electron correlation and their impacts on emergent phenomena in molecular and solid-state actinide materials. The purpose of this program is to understand f-element electronic structure and bonding and how it manifests itself in molecular and solid state structure and through its influence on spectroscopic and thermodynamic properties. Studies are directed at understanding 5f and 6d covalent mixing in metal-ligand bonding in light actinide complexes through a combination of synthetic chemistry, spectroscopic characterization, and theory and modeling to understand and predict the chemical and physical properties of actinide materials. Further studies are being undertaken to characterize collective and cooperative behavior within nanoscale domains with local compositions that deviate strongly from the average. The latter studies are primarily performed at OBES supported synchrotron or neutron sources. This multidisciplinary approach provides the scientific means to formulate rational approaches to solve complex actinide problems in a wide variety of environments to meet the next generation of needs in actinide science within the DOE complex. The systems under study are actinide species in aqueous and nonaqueous solutions, and solids.

FY 2014 HIGHLIGHTS

In FY14 the Los Alamos Heavy Element Chemistry (LANL HEC) program continued expanding understanding of unexpected covalency and electron correlation in actinide molecular science and in solid-state actinide materials. The success of the program in FY14 is demonstrated by the metrics summarized here. First and foremost are the LANL HEC quality manuscripts (over 20) that were published in high impact journals. Additionally, members of the LANL HEC team were invited to participate and organize international conferences in actinide science. LANL HEC has historically been a leader in the field of actinide chemistry, and consistent with this reputation members of the team were acknowledged within the community. This included Kiplinger's selection as the 2015 recipient of the F. Albert Cotton Award in Synthetic Inorganic Chemistry, Conradson named as an AAAS fellow, Kozimor being elected as the vice-chair of the Inorganic Gordon Conference, Martin honored with the 2nd Annual

Burris Cunningham Actinide Science award at LBNL, and Boncella's appointment as the chair of the ACS-Division of Inorganic Chemistry. The LANL-HEC program was also acknowledged by recruitment of its outstanding post-doctoral researchers into leadership roles at other institutions. For example, Neil Tompson accepted a position as an assistant professor at the Univ. of Penn., former post-doc Scott Daly was recruited to the Univ. of Iowa, Stefan Minasian was hired as a staff member at Lawrence Berkeley National Laboratory (LBNL), Matthias Löble was hired at Karlsruhe Institute of technology (KIT), and Angela Olson was converted to staff at LANL. Finally, the proximity of the team to programmatic efforts in national security facilitates transitioning LANL-HEC fundamental breakthroughs into operational capabilities. As testament, Kiplinger was honored in FY14 as a new Laboratory Fellow and Kozimor was recognized in the Los Alamos Award Program for outstanding contributions to the WIPP Investigation Project.

Actinide Chemistry

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Funding: \$3,117,000 (2014)

PROGRAM SCOPE

Berkeley Lab actinide research supports the role of the U.S. DOE as a key provider of fundamental science, science-driven solutions, and trained personnel to meet present and future national needs in actinide and nuclear chemistry. Objectives include understanding heavy element chemistry and physics at the atomic and molecular levels, and using this knowledge to address contemporary issues in actinide science. A central theme is 5f-orbital bonding and its impact on actinide chemistry and physics. Collaborative research ranges from exploring gas-phase actinide chemistry and synthesizing new actinide materials, to investigating 5f-element bonding, to elucidating electronic, magnetic, and reactivity characteristics of actinide molecules. Specific topics, including actinide complexation, solution chemistry, thermodynamics, and the chemical control of troublesome radionuclides, are pursued to overcome barriers to the advancement of nuclear energy. The research programs develop custom instrumentation for use with radioactive materials, including mass spectrometry, fluorimetry and calorimetry, and make intensive use of U.S. DOE synchrotron radiation light sources. Nuclear chemistry research explores chemical and nuclear properties of the heaviest elements. The comprehensive integrated approach to understanding actinide chemistry, as well as the emphasis on student involvement, make the program a unique effort in meeting the needs of the U.S. DOE in actinide science.

FY 2014 HIGHLIGHTS

The Berkeley Lab Heavy Element Chemistry research program has furthered fundamental understanding of the electronic structure, coordination chemistry, bonding and reactivity of f-electron materials,

spanning gas-phase to solution to solid state species. The first recognition of multiple sequential intramolecular energy transfer processes, leading to actinide luminescence sensitization by siderophore-like ligands forming macromolecular matrices, was established by single crystal X-ray diffraction and opens possibilities for new separations and sensors. Resonant hard X-ray spectroscopy provided the first evidence that details of f-orbital distribution, in addition to total f-orbital occupancy, dictate differences in Pu-based superconductors. These results indicate that differences in f-configuration fractions indeed exist, yet average to a similar total f-occupancy. Fragmentation of gas-phase complexes of Th⁴⁺, U⁴⁺, Np⁴⁺ and Pu⁴⁺ reflected variations in condensed phase redox chemistry across the actinide series and was shown to be a novel approach to explore actinide redox directly related to solution chemistry. The electronic structures of a new class of diamond-core U₅⁺²(U-O)₂ complexes, exhibiting strong exchange coupling between the U⁵⁺ centers, was unraveled in detail, clarifying the role of f-orbitals in magnetism and bonding of the actinides. Differences in f-element complexation were determined from the interactions of bis(2,4,4-trimethylpentyl)dithiophosphinate with Nd³⁺ and Cm³⁺ by a comparative study of thermodynamics and coordination modes. Unexpected bonding interactions were found by soft X-ray spectroscopy in two actinide sandwich molecules that have been at the center of debates regarding actinide covalency since the 1960s. The results show how f-element metal-carbon bonding can profoundly affect the reactivity and physical properties of organometallic molecules. A seaborgium carbonyl complex was synthesized and detected as part of a worldwide effort.

Heavy Element Chemistry

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Funding: \$2,539,000 (2014)

PROGRAM SCOPE

This program is providing fundamental knowledge of chemistry necessary for a predictive understanding of actinide behavior under environmental conditions and in basic separations scenarios of relevance to advanced technologies. The program has two primary foci, fundamental aspects of the chemical separation of actinides from fission products and the synthesis and characterization of new transuranic compounds. Our efforts are expressed in integrated and complementary projects centered on electronic properties, actinide-ligand interactions, structured phases, and solution interfaces. Within this context is an ongoing effort to develop the use of new-generation synchrotron radiation in support of actinide programmatic research. Our overall program is integrated through an emphasis on interactions that range from the atomic to the collective. We explore the structural correlations in solution and relate them to crystalline materials to understand the physical influences on bonding behaviors and energy partitioning. Single-ion properties such as formal potentials, optical behavior, and magnetic response

are quantified in detail. Complementing these studies are our efforts to understand molecular-level organization and aggregation of f-ion solutes in solution and the structures of solid phases that precipitate. On intermediate-length scales, we are characterizing solute and solvent organizations of supramolecular or nanoscale aggregates that can have a marked impact on solvent extraction systems. This effort is centered on structured solutions and deals largely with hydrophobic phases and aqueous/organic interfaces. Molecular dynamics calculations are coupled with X-ray scattering experiments from liquid-liquid interfaces to gain insight into molecular processes occurring at the interface during ion transfer between two immiscible liquids. These studies are providing insight into how to model and use molecular organization in targeted syntheses and separations.

FY 2014 HIGHLIGHTS

Novel results center on solution speciation, in which correlations were characterized that extend from the atomic through to the mesoscopic, probed in aqueous and organic phases as well as at liquid interfaces. Highlighting these efforts was the demonstration that solvent extraction, a common method for metal-ion separations, can be described using universality theories generally applicable to phase transitions in vastly different systems, from boiling liquids to traffic jams. Analyses of X-ray scattering data revealed how the complex structure and interactions in a solvent-extraction organic phase are modified as a function of extracted ion-pairs and temperature. Interactions between nanoscale aggregates change with temperature or solute concentration according to a simple universal critical function. This result considered as a foundational stone to a predictive solvent-extraction model that will improve the safety and efficiency of metal-ion separations from rare-earth refining to nuclear fuel reprocessing. Using a very different experimental approach, synchrotron X-rays were scattered from an interface designed to mimic a simple solvent-extraction system. We were able to demonstrate that a temperature-driven adsorption transition can turn an extraction on and off by controlling adsorption and desorption of extractant molecules at the interface. Lowering the temperature through this transition immobilizes the supramolecular complex at the interface. Under the conditions of our experiments, these complexes condense into a two-dimensional inverted bilayer, which was characterized with subnanometer spatial resolution. Raising the temperature above the transition leads to extraction as a result of desorption of the complexes from the interface into the bulk organic phase. This molecular-scale phenomenon has not previously been associated with solvent extraction and may have a fundamental role in the efficacy of this widely-used method of chemical separations.

EARLY CAREER: Periodicity and the Role of the 5f-Electrons at Protactinium

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Sr. Investigator(s):
Students: 2 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding: \$500,000 (2014)

PROGRAM SCOPE

The scope of this program is understanding the fundamental chemistry of protactinium in order to gain a quantitative, predictive knowledge of the periodic properties of early actinide chemistry and how it may be applied to separations chemistry fundamental to advanced nuclear fuel cycles. Our approach and hypotheses are inspired by the important interplay between the 5f and 6d electronic states in the

bonding of the early actinides, particularly the progressive periodic stabilization of the atomic 5f orbitals relative to the 6d orbitals moving from Th to heavier actinides, and the role it has on their chemistry. The overarching theme that drives this study is that at protactinium, the 5f and 6d orbitals are nearly degenerate in energy making Pa the first actinide where significant contributions from both these orbitals are made to the molecular bonding. Therefore, the relative contributions of the 5f and 6d electronic states to the bonding in Pa complexes depends on the chemistry of the Pa-ligand interaction and can be tuned between d- and f-character. Using prior experimental and theoretical observations of Pa chemistry, in addition to the periodic chemical properties and trends established across the periodic table to guide this investigation, we propose to study the chemistry of Pa coupling synthesis of model inorganic Pa compounds with solid- and solution-state structural characterization, and spectroscopic studies in order to quantify how the unique electronic structure of Pa manifests itself in its chemistry. It is expected that the results from the study proposed here will serve to inspire and lead new theoretical treatment of actinide electronic structure as it relates to the interplay of the f and d states in the early actinides.

FY 2014 HIGHLIGHTS

Efforts this year have focused on the preparation and investigation of a series of fluoride and peroxide complexes of protactinium(V). Synthetic campaigns have resulted in the preparation of a series of alkali metal and alkyl ammonium bearing fluoroprotactinate complexes, and a heretofore never reported species of protactinium peroxide. These complexes were subsequently used as model systems in our investigation of the solution speciation and structure of protactinium in aqueous hydrofluoric acid and hydrogen peroxide solutions using X-ray absorption spectroscopy performed at the Advanced Photon Source at Argonne National Laboratory, and laboratory based vibrational spectroscopy. Because we are interested in observing the influence that the participation of the d- and f-orbitals have on the chemistry of protactinium, we studied its transition metal homologues, niobium and tantalum, in a parallel and complementary set of experiments. The results from these experimental efforts have highlighted both similarities and differences among the chemistry of protactinium, the other early actinide elements, and the transition metals. These results have garnered attention from other chemists interested in quantifying the electronic properties and reactivity of these compounds both computationally and experimentally.

An Integrated Basic Research Program for Advanced Nuclear Energy Separations Systems Based on Ionic Liquids

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Mark Dietz; Wisconsin-Milwaukee, University of
Huimin Luo; Oak Ridge National Laboratory
Ilya Shkrob; Argonne National Laboratory
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Funding: \$424,000 (2014)

PROGRAM SCOPE

Future advanced nuclear energy systems will require significant changes in the way nuclear fuel is processed to achieve greater efficiency and reductions in waste sent to repositories, which are necessary for sustainable nuclear power generation. We expect that ionic liquids (ILs, or low-melting salts) will enable technologies to achieve these goals. ILs have unusual physical properties and process safety advantages compared to ordinary solvents. Their properties can be controlled by design as needed. This project explores the use of ionic liquids for nuclear separations processes with particular concern for their performance under ionizing radiation as found under operating conditions. A multidisciplinary team has been assembled to study the fundamental radiation chemistry of ionic liquids, to determine how that chemistry interferes with separations efficiency in ILs, to seek to prevent or mitigate such interference through substitution of ionic liquid components, and to design and create IL-based systems for more efficient and radiolytically-robust separations chemistry. Some of these systems may operate in novel ways that take advantage of unique IL properties. The goal is to replace current technologies with ones that allow more efficient use of resources and smaller environmental impacts, bringing us closer to a sustainable energy future.

FY 2014 HIGHLIGHTS

- We studied the radiation chemistry of ionic liquids (ILs) made with functionalized cations from cheap, readily available sources: choline, betaine and carnitine. They are the focus of separations schemes that exploit their upper critical solution phase behavior with water. Our EPR studies on choline salts explained the mechanism of “radiation hypersensitivity” of choline chloride, a controversial subject since Calvin’s 1953 discovery. In a first-of-its-kind experiment, the BNL LEAF facility’s mid-IR transient absorption system was used to observe the formation kinetics and yields of the choline radiolysis products vinyl alcohol and acetaldehyde, using their characteristic C=C and C=O stretching frequencies. (DOI: 10.1021/jp5049716)
- We showed that 1-benzylpyridinium cations and related derivatives are highly radiation-resistant cations due to charge delocalization in both the reduced and oxidized forms of the ILs. Pulse radiolysis and EPR data show that the excess electron and hole are stabilized in these ILs by formation of pi-electron sandwich dimers, similar to dimer radical cations of aromatic molecules. The charge delocalization dramatically reduces the yield of fragmentation by deprotonation and the loss of benzyl arms, thereby providing a path to radiation resistant ILs suitable for nuclear fuel processing. (DOI: 10.1021/jp408242b)
- We are exploring alternative IL-based systems for group separation of lanthanides from minor actinides, analogous to the TALSPEAK process but taking advantage of the unique features of ILs. In one case, the role of water was replaced by the IL betainium NTf₂. The complexant DTPA was incorporated into the IL by esterification with choline cation. Extractions against HDEHP in cumene showed excellent group separations for Ln over An. In another study, good rare earth separation was achieved when dialkylphosphate ILs were used as extractants in a process where hydrophobic IL replaced the hydrocarbon phase in TALSPEAK. (DOIs: 10.1021/ie4036719)

Photosynthetic Systems

Institutions Receiving Grants

Energy Transfer and Radiationless Decay in Light-Harvesting Proteins

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Students: 0 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding: \$160,000 (2014)

PROGRAM SCOPE

This project employs two-dimensional (2D) electronic spectroscopy and transient-grating spectroscopy with optical heterodyne detection to determine the structural and physical mechanisms that control and optimize the excitation energy transfer processes involved in photosynthetic light-harvesting. The research focuses on how carotenoids serve as mid-visible antenna chromophores that are capable of efficiently transferring excitation energy to chlorophyll molecules. The initial focus is on the question of how intramolecular charge-transfer (ICT) character develops upon optical preparation of carotenoid excited states. This issue is central to the mechanism for energy transfer from the dark carotenoid S_1 (2^1Ag^-) state to the chlorophyll Q_y state because the latter formally lacks any transition dipole strength. The research plan compares the photophysics of two carotenoids in solution, β -carotene and peridinin, to that of peridinin in the structurally well-characterized peridinin–chlorophyll a protein (PCP), a light-harvesting protein from marine dinoflagellates. This protein features energy-transfer pathways between four peridinin chromophores and one chlorophyll a chromophore in each of the two subunit domains of the protein. This work is intended to determine how the protein binding sites for peridinin optimize the rate of energy transfer to the chlorophyll acceptors by preparing excited-state conformations that favor the formation of ICT character. Optical heterodyne detection in transient-grating experiments provides the means to detect the formation and decay of the dark intermediate electronic states that are populated on an ultrafast timescale in carotenoids after optical preparation of the bright S_2 (1^1Bu^+) state. 2D spectroscopy allows the pathways of energy transfer and the sequence of intermediate states to be determined specifically.

FY 2014 HIGHLIGHTS

We have completed transient-grating experiments on β -carotene and peridinin in solution in parallel with studies of the peridinin-chlorophyll a protein (PCP). The experimental results have been analyzed with the aid of full simulations of the nonlinear optical response functions that contribute to the signals. Our findings support a new model for the nonradiative decay pathways of carotenoids in solution that includes ultrafast motions along torsional coordinates of the conjugated polyene backbone. Our model identifies the S_x intermediate state detected in previous work as a twisted structure, most likely with intramolecular charge-transfer (ICT) character. This state serves as the energy-transfer donor to the Q_x state of (bacterio)chlorophylls in light-harvesting proteins. Further, the energy-transfer donor to the Q_y state of (bacterio)chlorophylls is assigned to a S_1 state having a twisted and probably bent conformation with an enhanced ICT character; this structure may account for the S^* state detected in previous work.

The transient-grating studies of peridinin in different solvents show that nonradiative decay from the S_1 state obtains a conformationally displaced S_0 structure that exhibits a strongly solvent-dependent relaxation rate to the originally excited, ground-state conformation. This part of the work required observations of the dispersion component of the third-order nonlinear optical signal with optical heterodyne detection. In PCP, the results indicate that the binding site for peridinin optimizes the energy transfer yield to the chlorophyll a acceptor by favoring conformations of the conjugated polyene with twisted and bent conformations. These conformations promptly assume excited-states with ICT character after optical excitation.

Regulation of Thylakoid Lipid Biosynthesis in Plants

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Students: 1 Postdoctoral Fellow(s), 1 Graduate(s), 1 Undergraduate(s)
Funding: \$185,000 (2014)

PROGRAM SCOPE

Photosynthesis provides feed, food, and fuels through the conversion of sunlight into chemical energy. At the core of the light reactions of photosynthesis is an extensive membrane system inside plant chloroplasts into which the photosynthetic protein/pigment complexes are embedded. The long term goal is to gain a mechanistic understanding of the assembly and maintenance of the photosynthetic membrane in plants with a primary focus on its lipid constituents. The galactoglycerolipids mono- and digalactosyldiacylglycerol, MGDG and DGDG respectively, are the main polar lipid constituents of the photosynthetic membrane. Of these two, MGDG is only found in plastids. Establishment and maintenance of the photosynthetic membrane is a dynamic process throughout the life cycle of the plant and involves finely tuned mechanisms to adjust synthesis and breakdown of polar lipids, particularly in response to conditions adverse to growth. The turnover of the principal membrane lipid of the photosynthetic membrane, MGDG, is explored. Two biochemical processes are investigated that involve the recently discovered enzymes SENSITIVE TO FREEZING2 (SFR2) and PLASTID GALACTOLIPID DEGRADATION 1 (PGD1), which catalyze the recycling of MGDG derived diacylglycerol or acyl moieties, respectively, into triacylglycerol following the exposure to abiotic stresses. SFR2 is required for survival of freeze stress in *Arabidopsis* and PGD1 plays a role in the accumulation of triacylglycerols in the microalga *Chlamydomonas* following nutrient deprivation, but the function of its plant orthologs remain to be determined. The specific aims are (1) to determine the activation mechanism of SFR2 during freeze stress, (2) to explore the function of SFR2 in lipid remodeling in response to different abiotic stresses, and (3) to determine the function of plant PGD1-like lipases in lipid remodeling and abiotic stress responses.

FY 2014 HIGHLIGHTS

A detailed homology model of *Arabidopsis* SFR2 provided the basis for an in-depth structure-function analysis delineating the active site, the reaction mechanism and processivity. SFR2 is a novel type of processive galactosyltransferase using MGDG as a substrate and produces oligogalactolipids with up to six galactosyl residues. It is classified as a hydrolase but cannot hydrolyze any substrates tested. SFR2 is constitutively present in the cytosolic leaflet of the outer envelope membrane of chloroplasts but not

active under normal growth conditions. Experiments with isolated chloroplasts ruled out several possible factors, but identified a decrease in the pH and an increase in the concentration of magnesium ions as activating factors. It is hypothesized that freezing leads to a decrease of the cytosolic pH and an increase in the cytosolic magnesium concentration as the plastid envelope membranes are disrupted activating SFR2 and allowing it to repair and adjust the lipid composition of the envelope membranes. SFR2 is present in all plants. Inactivating SFR2 in cold sensitive tomatoes enhanced the sensitivity to salt and drought stress expanding the range of possible physiological roles of SFR2. The *Arabidopsis* genome encodes three PDG1 orthologs designated PDGL1-3. All three localize to the plastid, likely to different membranes: the inner and the outer envelope membranes and the thylakoid membrane. Active recombinant PGDL3 was produced and shown to have lipase activity removing unsaturated acyl-chains from the sn-1 position of specific chloroplast glycerolipid molecular species, e.g. phosphatidylglycerol with a 16:1 delta-3-trans acyl-chain in the sn-2 position. Double mutant combinations showed enhanced sensitivity to abscisic acid and a reduction in seed triacylglycerol content. It is hypothesized that PGDL lipases allows channeling of chloroplast lipid derived acyl groups into triacylglycerols under stress conditions that are currently being explored.

Molecular Mechanism of Action of the Cyanobacterial Orange Carotenoid Protein

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Students: 0 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding: \$370,000 (2014-2015)

PROGRAM SCOPE

All photosynthetic organisms contain a light-harvesting antenna system, which is how the organism absorbs sunlight so that the energy is stored ultimately in reduced carbon of biomass. Photosynthetic antenna systems are extremely diverse, in terms of structural organization and type of pigment utilized. In addition to the light absorption function of the antenna, it is essential for all photosynthetic organisms to have regulatory mechanisms that serve to protect them against excess light. This project centers on the Orange Carotenoid Protein that is found in photosynthetic cyanobacteria and serves to regulate energy collection in the major antenna complex, which is known as the phycobilisome. The Orange Carotenoid Protein binds a carotenoid molecule as the pigment. Research proposed here includes a variety of mechanistic studies on the isolated Orange Carotenoid Protein derived from genetically modified strains. We propose to develop a mutagenesis system for the Orange Carotenoid Protein and some subunits of the phycobilisome and analyze a series of mutants to better understand how the protein environment of the phycobilisome contributes to the energy regulation process. We also plan to examine the Orange Carotenoid Protein photoactivation and deactivation pathway. The results of this research project should give us a much improved understanding of the photoactivation mechanism of this important photoprotection process at the molecular level and also improve our understanding of its physiological roles in cyanobacterial adaptation to changing environmental conditions.

FY 2014 HIGHLIGHTS

This is a new project initiated in 2014 so results are just beginning to be obtained. We are in the process of testing our mechanism of action of the orange carotenoid protein that involves a light-induced dimer to monomer transition. Chemical labeling mass spectrometry results support this mechanism, but more testing is underway.

Photosystem II: Structure and Assembly

Institution: Louisiana State University
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Students: 2 Postdoctoral Fellow(s), 1 Graduate(s), 2 Undergraduate(s)
Funding: \$555,000 (2014-2016)

PROGRAM SCOPE

Elucidation of the functional properties and structural organization of membrane protein complexes is one of the central objectives of current biochemical investigation. One of the most intriguing aspects of membrane function is its role in the mediation of energy transduction in photosynthetic organisms. Light energy, which is the product of a most violent physical process, fusion, is transformed into biological energy equivalents utilized by the photosynthetic cell. This photosynthetic process provides both the carbohydrate that lies at the base of virtually all food chains and, as a byproduct, all of the atmospheric oxygen utilized by heterotrophic organisms. One factor which limits photosynthetic productivity is photoinhibition. The production of reactive oxygen species by Photosystem II is inherently damaging to the photosystem. The sites of production of the reactive oxygen species which specifically damage Photosystem II, however, have not been determined. Our first goal in this proposal is to elucidate the amino acid oxidative modifications which result from the reactive oxygen species produced by Photosystem II. In these studies we will use stable isotopic labeling with ^{18}O coupled with high-resolution mass spectrometry. Second, the Photosystem II of higher plants contains a different palette of extrinsic membrane protein components than does cyanobacterial Photosystem II. The locations of these components (a second copy of PsbO, as well as PsbP and PsbQ) within the higher plant photosystem have not been determined. In this proposal we will use a combination of radiolytic footprinting performed at the J. Bennett Johnston, Sr. Center for Advanced Microstructure & Devices synchrotron and *in vitro* protein crosslinking to elucidate the location and orientations of these important protein components of higher plant Photosystem II. Mass spectrometry also plays a vital role in these studies.

FY 2014 HIGHLIGHTS

Published Research: We published three papers during this time frame, with a fourth paper submitted (and subsequently published in PNAS). These are listed below.

1. Bricker, T.M., Bell, A.J., Tran, L., Frankel, L.K. and Theg, S.M. "Photoheterotrophic Growth of *Physcomitrella patens*". *Planta* 239, 605-613 (2014).
2. Roose, J.L., Frankel, L.K. and Bricker, T.M. "The PsbP-Domain Protein 1 Functions in the Assembly of Lumenal Domains in Photosystem I". *Journal of Biological Chemistry* 289, 23776-23785 (2014).

3. Zhang, P., Frankel, L.K. and Bricker, T.M., "Integration of apo- α -phycocyanin into phycobilisomes and its association with FNRL in the absence of the phycocyanin α -subunit lyase (CpcF) in *Synechocystis sp.* PCC 6803". Plos One 9, e105952 (2014).
4. Mummadisetti, M.P., Frankel, L.K., Bellamy, H., Sallans, L., Goettert, J.S., Brylinski, M., Limbach, P.A. and Bricker, T.M. "Use of Protein Crosslinking and Radiolytic Labeling to Elucidate PsbP and PsbQ Interactions within Photosystem II of Higher Plants." Proceedings of the National Academy of Sciences (USA), in Revision during the time period highlighted.

Unpublished Research:

1. We have made significant progress in isolating and characterizing protein cross linked products containing PsbO, PsbP and PsbQ. These have been identified using both the 0-length cross linker EDC and the bifunctional cross linker BS3 (span 11.4 Å). We are currently analyzing these with high resolution FTICR MS/MS.
2. Photoinhibition experiments with both red and white light have been performed in the presence of either ^{18}O -dioxygen or ^{18}O - H_2O . These samples will be analyzed by FTICR MS/MS to identify sites of oxidative modifications.
3. We have isolated a highly enriched PS I-LHC I -LHC II membrane fraction. The LHC II appears to be strongly energetically coupled to the PS I reaction center and the complex is isolated in very high yield (mgs of chlorophyll yields).

Multi-Frequency Pulsed EPR Studies of the Photosystem II Oxygen Evolving Complex

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 Sr. Investigator(s):
 Students: 1 Postdoctoral Fellow(s), 1 Graduate(s), 3 Undergraduate(s)
 Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

The primary goal of this grant is to better understand the catalytic mechanism of the Mn-Ca water oxidizing/oxygen evolving center of Photosystem II. This multimetal center carries out the four electron oxidation of two water molecules, producing bio-activated electrons and protons, with molecular oxygen released as a byproduct. Each of the four oxidation steps in the catalytic cycle is driven by photon induced electron transfer, which allows us to step through the successive intermediates of the "S-state" cycle using saturating laser flashes. We need to better understand the electronic structure of this complex metal cluster and its ligand environment as it advances through the cycle in order to understand how this unique natural catalyst carries out this crucial chemistry. We are using multifrequency pulsed electron paramagnetic resonance (EPR) spectroscopy as our experimental approach. EPR is a powerful tool for studying paramagnetic intermediates of enzymes that use metals or organic radicals in their reaction mechanisms, and the Mn cluster of the PSII OEC is a prime example, with S_0 and S_2 showing strong Mn EPR signals. The resolution of conventional continuous wave (CW) EPR is limited however, and non-linear pulsed echo methods have therefore been used to achieve resolution enhancement of two or three orders of magnitude. We carry out all the standard pulsed EPR techniques used to measure magnetic hyperfine interactions between electron spins and magnetic nuclei (such as ^{55}Mn , ^{13}C , ^{14}N , ^1H , and ^2H). These include electron spin echo envelope modulation methods in one and two dimensions (ESEEM and HYSCORE), pulsed electron nuclear double resonance (ENDOR), and their

variants. These methods give a direct probe of the electronic structure of the OEC as a function of S-state.

FY 2014 HIGHLIGHTS

Oyala, P. H., T. A. Stich, J. A. Stull, F. Yu, V. L. Pecoraro, and R. D. Britt. Pulse EPR Studies of the Interaction of Methanol with the S₂ state of the Mn₄CaO₅ cluster of Photosystem II. (2014) *Biochemistry*, 53:7914-7928. This 2014 paper uses pulsed EPR to study methanol binding (via ¹³C-labeled MeOH) in the S₂ state of the OEC. We conclude based on measurements on the OEC and related Mn model compounds that methanol does not bind directly to Mn, but is likely bound instead to the Ca of the OEC or possibly in one of several adjacent water sites.

Structure/Function Studies of Photosystem II

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Sr. Investigator(s):
Students: 1 Postdoctoral Fellow(s), 3 Graduate(s), 0 Undergraduate(s)
Funding: \$230,000 (2014)

PROGRAM SCOPE

Despite significant recent progress, the mechanism of water oxidation in photosystem II (PSII) remains the least understood aspect of photosynthetic electron transport. The long-term objectives of this project are to develop an understanding at the molecular level of the structure and assembly of the active site of water oxidation, the catalytic mechanism of water oxidation, the electron-transfer properties of PSII, the damaging side reactions that occur in the process of water oxidation and the mechanisms by which the secondary electron-transfer reactions of PSII involving carotenoids moderate the damaging side reactions. The recent 1.9 Å resolution X-ray crystal structure of PSII provides a detailed architecture of the oxygen-evolving complex (OEC) and the surrounding amino acids. Building on the new structural information, this project uses biophysical studies in conjunction with manganese model chemistry to characterize the function of PSII. The specific aims of the current project are: (1) to characterize the redox functions of carotenoids and the secondary electron-transfer reactions in PSII by (a) studying site-directed mutants of PSII in which amino-acid residues predicted to perturb cofactors in the secondary electron-transfer pathways are changed, and (b) redirecting electron transfer on the acceptor side of PSII in order to utilize the electrons liberated from water oxidation by PSII for photoelectrochemical fuel formation; and (2) to carry out structure-based experiments on PSII to characterize the function of specific residues and the mechanism of the OEC by (a) investigating the function of chloride in oxygen evolution by studies of anion-substituted PSII and site-directed mutants of D2-Lys317 and (b) using oxygen isotope studies to gain insight into how the substrate waters are bound and activated for reaction in the OEC.

FY 2014 HIGHLIGHTS

To probe the side-path electron-transfer reactions of photosystem II (PSII) and their role in photoprotection (aim 1), site-directed mutations around the binding pocket of the D2 carotenoid (Car-D2) were made in *Synechocystis* sp. PCC 6803 in collaboration with Peter Nixon at Imperial College.

Studies of PSII core complexes by near IR and EPR spectroscopy show that oxidation of Car-D2 is the initial step in secondary electron transfer and analyses of mutant cell growth link this reaction to photoprotection. X-ray crystallography has revealed that chloride binds as an ion-pair with D2-K317 at a distance of 6-7 Å from the Mn₄Ca cluster in the O₂-evolving complex (OEC). To probe the role of chloride in PSII (aim 2), mutations at the D2-K317 site were made in *Synechocystis sp.* PCC 6803 in collaboration with Richard Debus at the University of California, Riverside. FT-IR and EPR spectroscopy, together with oxygen-evolution measurements, on PSII core complexes support our proposal that the function of chloride is to modulate proton transfer. Notably, the first chloride-independent water-oxidizing PSII was engineered by making the D2-K317A mutation. In addition, we completed a study on the inhibitory effect of nitrite on PSII. Nitrite has previously been reported to be a functional substitute for chloride, but this seems unusual owing to nitrite's chemical dissimilarity to chloride and its potential for redox activity. Our results show that nitrite is, in fact, an inhibitor of PSII. These results clarify the effect of nitrite and provide new information on the role of anions in photosynthetic water oxidation. We have also collaborated with the groups of Victor Batista (Yale University) and Marilyn Gunner (City College of New York) on computational modeling of PSII. Computational models have been developed and used to calculate pK_as and oxidation midpoint potentials of oxomanganese complexes that model the OEC and the structure of the S₀ state of the OEC.

Light Energy Transduction in Green Sulfur Bacteria

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Funding: \$292,000 (2014)

PROGRAM SCOPE

Green bacteria characteristically occur in energy-limited environments that at extraordinarily low light intensities. Nevertheless these organisms often grow rapidly because they have exceptional light harvesting capabilities. This is because they use chlorosomes, the most efficient light-harvesting organelles known, for light harvesting. We are studying chlorosomes, and the reaction centers to which they are coupled in specific cases, in organisms that come from very different environmental niches, in order to understand specific adaptations to specific light conditions. An important recent achievement was the isolation of multiple axenic strains of *Chloracidobacterium thermophilum*, the first chlorophototrophic member of the phylum Acidobacteria. We are also continuing to characterize chlorosomes in *Chlorobaculum tepidum* and *Cba. limnaeum*, which employ different types of bacteriochlorophyll in their chlorosomes. To investigate the ecophysiology and metabolic capabilities of green bacteria, we employ genome sequencing, comparative bioinformatics and genomics, genetics, biochemistry, biophysics, and structural biology approaches. Comparisons of the properties of chlorosomes and homodimeric Type-1 RCs of organisms inhabiting anoxic (*Cba. tepidum* and *Cba. limnaeum*) and oxic (*Ca. C. thermophilum* and *T. aerophilum*) environments should reveal important adaptations to these two very different niches and will provide new information about the evolution of photosynthesis as well as the design principles for artificial photosynthesis.

FY 2014 HIGHLIGHTS

After finally obtaining an axenic isolate of *Chloracidobacterium thermophilum* in 2013, we spent most of the past year characterizing the physiology and metabolism of this novel chlorophototrophic bacterium. *Cab. thermophilum* requires all three branched chain amino acids, L-lysine, bicarbonate, vitamin B₁₂, and a reduced sulfur source (e.g., thioglycolate for growth). It is a microaerophile and grows best at about 50 micromolar oxygen. Once we understood the optimal growth conditions and requirements well, it has been possible to isolate additional isolates by direct plating from dilutions of mat samples. Characterization of these new isolates suggests that we have isolated either new species or at least ecological species of this organism. We have continued our structural studies on chlorosomes, and have characterized the chlorosomes of the *bchR* mutant of *Chlorobaculum tepidum* together with the group of Joergen Koehler. The results show that the bacteriochlorophylls (BChls) in this mutant have a different suprastructure than those in the wild type and other mutants we have characterized. We have produced mutants in genes encoding enzymes required for the synthesis of BChl e. Structural studies on uniformly ¹³C-labeled chlorosomes are in progress with collaborators in the laboratory of Dr. Huub de Groot. We also completed studies to characterize the photophysical properties of BChl e and BChl f. Finally, we have made some progress on our attempts to isolate an aerobic green sulfur bacterium, *Candidatus Thermochlorobacter aerophilum*, from microbial mats in Yellowstone National Park, WY.

Genetic and Metabolic Integration of the Carbon Concentrating Mechanism with the Light and Dark Reactions of Oxygenic Photosynthesis

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Funding: \$260,000 (2014-2015)

PROGRAM SCOPE

Cyanobacteria are considered as ideal vehicles for numerous bioengineering applications ranging from CO₂ mitigation to the production of biofuels and chemicals. The acquisition of inorganic carbon (CO₂, HCO₃⁻) very often limits photosynthetic performance in natural systems, including cyanobacteria. This limitation is likely to be even more acute in engineered systems that may have proportionally higher demands for inorganic carbon relative to other nutrients. To overcome this limitation, cyanobacteria possess a CO₂-concentrating mechanism (CCM) that is capable of utilizing cellular energy to acquire and concentrate CO₂ and bicarbonate from the environment. The overall objective is to better understand the cyanobacterial high affinity CCM and its integration with the reactions of oxygenic photosynthesis. Work is testing the general hypothesis that the genetic integration of the CCM with the light and dark reactions of photosynthesis is achieved mainly through physiological interactions involving metabolic intermediates that connect different photosynthetic processes. During the previous funding period, transcriptional control of inducible, high affinity, CCM genes was found to be modulated by key photosynthetic metabolites, including NADP⁺ and α-ketoglutarate. These metabolites, in turn, modify the DNA binding activity of regulatory proteins. These findings reveal a homeostatic regulatory mechanism that adjusts the CCM to changes in the demand for CO₂ based upon internal metabolic cues that themselves responding to changing environmental conditions, notably, inorganic carbon availability

and light intensity. Building on this progress, current experiments investigate the mechanisms of regulation and the unique CO₂ uptake enzymes that are being regulated.

FY 2014 HIGHLIGHTS

Molecular genetic and physiological analyses we applied to understand the fluctuations in the identified regulatory metabolites under changing light and Ci-availability. Analysis of cells experiencing Ci limitation reveals systematic changes associated with physiological adjustments and a trend towards the quinone and NADP pools becoming highly reduced. This was followed by a series of changes ranging from increased dissipation of the light energy to changes due to the induction of the high affinity CCM. The results are consistent with the proposed regulation of the CCM and provide new information on the nature of the Chl and NADPH fluorescence induction curves. The unique CO₂ uptake enzymology remains to be clarified, although it is known to involve variants of the Type-1 NAD(P)H dehydrogenase (NDH-1) complexes that have additional subunits. A mutagenesis system is being developed to probe the structure-function relationships of the NDH-1_{3/4} complexes for CO₂-hydration activity. This enhances the on-going effort to use synthetic techniques to manipulate the cyanobacterial CCM. An optimization computer model for autotrophic cyanobacterial growth, the autotrophic replicator model (ARM), was developed. The present model describes autotrophic growth in terms of the allocation of protein resources among core functional groups including the photosynthetic electron transport chain, light harvesting antennae, and the ribosome groups. This model will help us connect our molecular genetic and physiological analyses with the metabolomic studies of our NREL collaborators.

Investigations into Proteins Affecting Chloroplast Function

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Funding: \$75,000 (2014)

PROGRAM SCOPE

Capture of light energy into chemical energy and production of plant biomass for biofuels depend on the optimal development and functioning of the higher plant chloroplast and appropriate distribution and utilization of carbohydrates. We propose that these two functions require different members of the pfkB super-family of carbohydrate-like kinases, which are related to an *E. coli* phosphofructokinase. However, in plants this single gene has expanded consisting of 23 members in *Arabidopsis*. Functions for few are known. Seven have been either documented or postulated as kinases on adenosine (2), NAD, pyridoxal, thiamine, fructose or myo-inositol. Another was implicated in chloroplast function, but mechanism is unclear. Sixteen PfkB proteins remain uncharacterized. The long-term goals are to understand the function of these proteins through isolation and characterization of mutants, identification of subcellular localization and activity assays. Multiple PfkB proteins localize to chloroplasts. Chloroplasts capture light energy and convert it into chemical energy in the form of reduced carbon compounds. We previously focused on two PfkB proteins FLN1 and FLN2 found in chloroplast transcription complexes from proteomic analyses by other labs. No kinase activity has been demonstrated and their role in chloroplast transcription is enigmatic. Our analysis of loss-of-function mutants revealed their partially overlapping significant roles in chloroplast transcription and biogenesis.

This work was published with DOE support (Gilkerson *et al*, 2012). Fructokinase activity is thought responsible for fructose assimilation. However, the sum of fructokinase activities in a plant is unknown. Objectives of the current research are two-fold. One is to understand how FLN proteins regulate transcription of chloroplast photosynthetic genes. The other goal is to identify functions for the remaining PfkB proteins whose functions are unknown with an emphasis on putative fructokinase proteins.

FY 2014 HIGHLIGHTS

We conducted a phylogenetic analysis and identified six proteins that clade with active fructokinase. Another showed similarity to ribokinase. One is a pseudogene. We identified subcellular locale for all but 2. We isolated insertion mutants in 10 genes (2 have no insertions and another lab is studying 1). RNA analyses were performed and all suggest some loss of function. We are using Crispr system to knock-out function of two genes and to make multiple mutants in the fructokinase clade. One double mutant in fructokinase genes is made and under analysis. We focused on ribokinase. It has a putative transit peptide and we demonstrated that it localizes to chloroplasts. We determined that ribokinase mutant seedlings are hyper-sensitive to growth on ribose compared to wild-type. These data strongly indicate a biological function for ribokinase in phosphorylating ribose. We isolated *E. coli* ribokinase and demonstrated activity; however, we have not yet demonstrated activity with *Arabidopsis* ribokinase. We expressed several fructokinase proteins in *E. coli* and demonstrated activity for two. For our analysis of FLN proteins in chloroplast function, we made significant progress. We expressed FLN proteins in *E. coli* and are using recombinant protein for biochemical analyses. We discovered that FLN1 and FLN2 interact in an ATP-dependent manner, while FLN2 interacts independent of ATP. Most exciting is our observation that FLN1-FLN2 heteromers are preferred over FLN2 homomers in high ATP. This has led to our hypothesis that ATP controls assembly of the transcriptional complex. We expressed fluorescently tagged FLN proteins in tobacco and demonstrated that their interaction is ATP-dependent in the chloroplast. Thus, we are completing the final replicas and controls to prepare a manuscript on our findings.

Signal Transduction Pathways that Regulate CAB Gene Expression

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PROGRAM SCOPE

Chloroplasts of higher plants contain about 3000 proteins of which more than 95% are encoded by nuclear genes. This necessitates a tight coordination of gene expression that involves two-way signaling between these spatially separated genomes. Thus, while plastid differentiation and development are largely under nuclear control, developmentally arrested or damaged plastids can regulate expression of a subset of nuclear genes via retrograde signaling pathways. Multiple retrograde signals have been proposed, but almost nothing is known of their signaling pathways. In previous years of this DOE-funded study, we performed a number of genetic screens that implicated the chloroplast-localized tetrapyrrole biosynthesis pathway as the source of both positive and stress-related retrograde signals. However, the

mechanisms by which tetrapyrrole intermediates or a secondary signal exit the plastid and the components by which this signal is relayed to promoters in the nucleus are mostly unknown. The goal of this proposal is to define the signal(s) and signaling pathways from chloroplasts that regulate nuclear gene transcription. The proposed studies will integrate genetic, genomic, molecular, and biochemical approaches in an effort to:

- (1) Test the hypothesis that GUN1, a chloroplast PPR protein, is a regulator of tetrapyrrole synthesis;
- (2) Further explore our finding that a specific pool of heme is the source of a positive signal that chloroplasts are functional;
- (3) Continue genetic and biochemical dissection of the signaling pathway(s) initiated from changes in photosynthetic electron transport redox state in response to excess light.

FY 2014 HIGHLIGHTS

- GUN1: GUN1 contains 10 PPRs and a second domain called the SMR (small MutS-related) domain. In bacteria, the SMR domain has endonuclease activity. We generated recombinant GUN1 protein and mutant proteins and showed that GUN1 contains nuclease activity. In plants, all 10 PPR domains and the nuclease activity are required for its function. Using whole genome RNA-sequencing analysis and genetic epistasis studies, we concluded that GUN1 acts in the same pathway as GUN2-6, but also acts in at least two other retrograde signaling pathways.
- High light stress screen: A distinct signaling pathway mediates signals derived from the reduction/oxidation (redox) state of the photosynthetic electron transfer chain (PET) and affects both photosynthesis-related and stress-related genes. Several studies have provided evidence for a role of the redox state of the PQ pool as a sensor of high light and a regulator of nuclear gene expression. We used a reporter gene fusion to identify mutants defective in the response to high light stress, and found genes involved in both early and late phases of the response. Early on, 3 heat shock factors (HSFs) of greater than 20 found in the genome play an important role in this process. For later responses, we are currently working through our mutant collection to clone genes. So far, we have identified mutations in 4 genes involved in later phases of light stress, including: cryptochrome, two RNA processing enzymes, and a co-activator. We want to order the genes into a regulatory network.
- A chloroplast quality control pathway. We identified a mutant that accumulates high levels of singlet oxygen—leading to selective chloroplast degradation and chloroplast-induced cell death. We performed a suppressor screen and cloned 8 genes, which when mutated suppress the cell death phenotype. One of these encodes an E3 ligase that marks chloroplasts with ubiquitin. We now want to know if these marked chloroplasts are selectively degraded.

Disruption of the CO₂ Concentrating Mechanisms in C₄ Plants: Implications for CO₂ Fixation and Photosynthetic Efficiency during C₄ Photosynthesis

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Funding: \$170,000 (2014)

PROGRAM SCOPE

The specialized biochemistry and leaf anatomy of C₄ plants results in a high CO₂ concentration within the leaf, significantly increasing photosynthetic energy use efficiency compared with C₃ plants. However, the efficiency of the CO₂ concentrating mechanism in C₄ plants can be negatively affected by environmental conditions but it is not understood how C₄ photosynthesis responds to optimize photosynthetic efficiency. For example, changes in the activity of key C₃ and C₄ cycle enzymes and the cell wall properties may alter leakiness, defined as the ratio of CO₂ leak rate out of the bundle sheath to the rate of CO₂ supplied by the C₄ cycle, through changes in the C₃/C₄ cycle capacity and the permeability of CO₂ diffusion. Understanding how the coordination of the C₃ and C₄ cycles, and the diffusion of CO₂ from the bundle sheath cells influences the efficiency of the CO₂ concentrating mechanism in C₄ plants is critical for accurately modeling the yields of C₄ crops under future climatic conditions. Additionally, this information is important for optimizing the biochemical and structure features of potential C₄ plants for high photosynthetic efficiency while modifying cell wall properties to enhance processing for biofuel production. The research in this proposal is expected to increase our understanding of the photosynthetic conversion of solar energy into chemical energy, particularly how changes in the biochemical capacity and structural properties of the leaf influence the photosynthetic efficiency of CO₂ fixation in C₄ species. The overall objective of our research is to determine how changes in the capacity of the C₃ and C₄ cycles and bundle sheath cell wall properties determine the photosynthetic efficiency of the CO₂ concentrating mechanism in C₄ plants. Our central hypothesis is that the efficiency of the CO₂ concentrating mechanism in C₄ plants is optimized through balancing the activity of the C₃ and C₄ cycles with the structural properties of the bundle.

FY 2014 HIGHLIGHTS

Seven manuscripts were published in 2014 that acknowledge our BES funding. In 2014 we generated stable transgenic *Setaria viridis* that we are currently characterizing. Due to technical issues the development of these lines took longer than we anticipated; however, we are now position to finish up this research. Additionally, in 2014 we collected and analyzed data for four manuscripts on the temperature response of C₄ photosynthesis that are in preparation for submission in early 2015.

1. Gandin A., Koteeva N., Voznesenskaya E., Edwards G. Cousins A.B. (2014) Temperature response of the photosynthetic machinery in the C₃-C₄ intermediate *Salsola divaricate*. *Plant Cell and Environment* 37:2601-2612
2. von Caemmerer S., Edwards G.E., Koteyeva N., Cousins A.B. (2014) Single Cell C₄ photosynthesis in aquatic and terrestrial plants: a gas exchange perspective. *Journal of Aquatic Botany* 118:71–80
3. von Caemmerer S., Ghannoum O., Cousins A.B. (2014) Carbon isotope discrimination as a tool to explore C₄ photosynthesis. *Journal of Experimental Botany* DOI:10.1093/jxb/eru127
4. Kromdijk J., Ubierna N., Cousins A.B. Griffiths H. (2014) Bundle sheath leakiness in C₄ photosynthesis: a careful balancing act between CO₂ concentration and assimilation. *Journal of Experimental Botany* 65:3443-3457
5. Studer A., Gandin A., Kolbe A., Cousins A.B. Brutnell T. (2014) Carbonic anhydrase does not limit photosynthesis in *Zea mays* under current atmospheric CO₂ conditions. *Plant Physiology* 165:608-617
6. Sun W., Ubierna N., Ma J.Y., Walker B., Kramer D., Cousins A.B. (2014) The coordination of C₄ photosynthesis and the CO₂ concentrating mechanism in *Zea mays* and *Miscanthus× giganteus* in response to transient changes in light quality. *Plant Physiology* 164:1283-92
7. Stutz S.S., Edwards G.E., Cousins A.B. (2014) Single-cell C₄ photosynthesis: efficiency and acclimation of *Bienertia sinuspersici* to growth under low light *New Phytologist* 202:220-32

EARLY CAREER: Thylakoid Assembly and Folded Protein Transport by the Tat Pathway

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Funding: \$150,000 (2014)

PROGRAM SCOPE

The research objectives are to study the mechanisms of protein transport into the lumen of thylakoids by the chloroplast Twin Arginine Transport (cpTat) pathway by (1) identifying the cpTat component(s) that interact with the mature domain of the precursor during transport, (2) determining the organization of the cpTat translocon, and (3) comparing topology of cpTat component, Tha4, in thylakoids during active transport and at rest. This particular protein transport pathway is predicted to translocate ~50% of the lumen proteins. Understanding cpTat system mechanism in chloroplasts will lead to a better understanding of the biogenesis of photosynthetic membranes potentially providing a means to engineer photosynthetic complexes into synthetic membranes for energy production.

FY 2014 HIGHLIGHTS

Proteins destined for the thylakoid lumen of chloroplasts are nuclear-encoded, synthesized in the cytoplasm, and must cross three membranes en route to their final destination. The chloroplast Twin Arginine Translocation (cpTat) system facilitates transport of about half of all proteins that cross the thylakoid membrane in chloroplasts. Known mechanistic features of the cpTat system are drastically different from other known translocation systems, notably in its formation of a transient complex to transport fully folded proteins utilizing only the protonmotive force for energy. However, key details such as the structure and composition of the translocation pore are still unknown. Our aims were to identify the composition of the cpTat translocation complex as well as probe the topology of two of the membrane proteins, Tha4 and Hcf106, involved in the cpTat translocation apparatus. Previously, we identified points of contact between precursor and Tha4 and demonstrated topology of Tha4 in non-transport active thylakoid and in transport active thylakoid. Currently, we are determining the points of contact between Tha4 and the precursor as it transports. These data strongly implicate Tha4 as a major component in the translocation pore. We are also actively expanding our investigation of Tha4 during transport to get a complete picture of the changes the molecule undergoes during transport of precursor. We are addressing Hcf106 organization in the thylakoid and indirectly interaction with cpTatC. Further we are gaining insight into the general mechanism of spontaneous insertion of a protein into the membrane through biophysical studies of the Hcf106 protein and peptides. We would then apply this knowledge to the insertion of several thylakoid proteins, which also seem to follow a spontaneous insertion pathway.

Membrane-Attached Electron Carriers in Photosynthesis and Respiration

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

The long-term goal of our work is to define the nature, mechanism of function, and biogenesis of cytochromes (cyt). Cyts and cyt containing complexes are ubiquitous electron carriers in energy transduction pathways. They are essential for cellular processes for chemical energy production (ATP). We seek a mechanistic understanding of these energy transduction pathways that include photosynthesis (Ps) and respiration (Res). Understanding how cells make and maintain (maturation, assembly and repair) cyts c is a fundamental process with major significance for efficient biological energy conversion. Our experimental model for these studies is the facultative phototrophic *Rhodobacter* (*R.*) species. Our work investigates molecular organizations of “hard-wired” and “soft-wired” ET complexes in membranes, including biogenesis of c-type cyts. The overall process involves the attachment of a covalent heme cofactor to an apocyt c (cyt c maturation, Ccm) to yield a mature holocyt c, and the assembly of holocyts c into functional multi-subunit membrane complexes. The Ccm process is found virtually in all living organisms, and the specific Ccm (System I) that we study occurs in bacteria, archaea, mitochondria of plants and red algae. Our previous work uncovered the *R. capsulatus* CcmI, CcmE, CcdA components of Ccm, and the DsbA-DsbB components that interact with Ccm. Ongoing work is focused on deciphering the protein-protein interactions between the apocyt c and heme as substrates, and CcmI, CcmH, CcmG and CcmHFI complex as chaperones and catalysts of Ccm. We believe that these studies are relevant to energy biosciences and their applications. They are also of broad biological significance, as the biogenesis components are part of major cellular functions, including protein translocation, extra-cytoplasmic protein folding and degradation, redox homeostasis, metal trafficking and insertion into proteins. Their understanding is of utmost importance for our mastery of photosynthetic and respiratory electron transport.

FY 2014 HIGHLIGHTS

- Studies involving the interactions between heme and apocyt c2, apocyt c2 and chaperone CcmI as well as the substrate specificity of CcmI in respect to different c-type apocyts are being completed.
- Studies related to the role of the thiol oxidation-reduction loop that occurs during Ccm are being initiated.

FTIR Studies of Photosynthetic Oxygen Production

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Funding: \$499,177 (2014-2016)

PROGRAM SCOPE

The project's scope is to characterize the dominant water access and proton egress pathways that link the oxygen-evolving Mn_4CaO_5 cluster in Photosystem II (PSII) with the thylakoid lumen. The Mn_4CaO_5 cluster provides nearly all atmospheric oxygen on Earth. The cluster accumulates oxidizing equivalents in

response to light-driven photochemical events within PSII and then oxidizes two molecules of water to oxygen in the final step of a five-step cycle. Water oxidation is an extremely difficult chemical reaction, both thermodynamically and kinetically. The Mn_4CaO_5 cluster catalyzes this reaction far more efficiently than any synthetic catalyst because its protein environment controls the cluster's reactivity at each step in the catalytic cycle. This control is accomplished by precise choreography of the proton and electron transfer reactions associated with water oxidation and by careful management of both substrate (water) access and proton egress. The project's overall goal is to identify the amino acid residues that are responsible for this control and to determine the role of each. The project's specific goals are (1) to further delineate the dominant water access and proton egress pathways that link the Mn_4CaO_5 cluster with the thylakoid lumen and (2) to characterize the influence of specific residues on the water molecules that serve as substrate or as participants in the networks of hydrogen bonds that make up these pathways. Proton egress through these pathways provides the thermodynamic driving force for oxidizing the Mn_4CaO_5 cluster in its higher oxidation states. The project's primary investigative tool is infrared (IR) spectroscopy. Both FTIR difference spectroscopy and time-resolved IR spectroscopy are being used to characterize mutant PSII core complexes containing single amino acid substitutions of residues identified crystallographically or computationally as potentially participating in these networks or otherwise interacting with the Mn_4CaO_5 cluster.

FY 2014 HIGHLIGHTS

There is growing evidence that D1-D61 is the initial residue of a dominant proton egress pathway linking the oxygen-evolving Mn_4CaO_5 cluster to the thylakoid lumen. This residue interacts directly with water molecules in the first and second coordination spheres of the Mn_4CaO_5 cluster. During FY 2014, we explored the influence of D1-D61 on the water reactions accompanying oxygen production by characterizing the FTIR properties of the D1-D61A mutant of the cyanobacterium, *Synechocystis sp.* PCC 6803. On the basis of mutation-induced changes to the carbonyl stretching region near 1747 cm^{-1} , we concluded that D1-D61 participates in the same extensive networks of hydrogen bonds that have been identified previously by FTIR studies. On the basis of mutation-induced changes to the weakly hydrogen-bonded O–H stretching region near 3600 cm^{-1} , we concluded that D1-D61 interacts with water molecules that are located near the chloride ion that is coordinated by D2-K317 ion and that deprotonate or participate in stronger hydrogen bonds as a result of oxidizing the Mn_4CaO_5 cluster to its S_2 and S_3 oxidation states. On the basis of the elimination of a broad feature between 3100 and 2600 cm^{-1} , we concluded that the highly polarizable network of hydrogen bonds whose polarizability or protonation state increases during the formation of the Mn_4CaO_5 cluster's S_2 oxidation state involves D1-D61. On the basis of the elimination of features in the D–O–D bending region near 1210 cm^{-1} , we concluded that D1-D61 forms a hydrogen bond to one of the H_2O molecules whose H–O–H bending mode changes in response to formation of S_2 oxidation state. The elimination of this H_2O molecule in the D1-D61A mutant provides one rationale for the decreased efficiency of the water oxidation in this mutant.

Revealing and Applying the Principles of Water Oxidation by Oxygenic Photosynthesis

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Funding: \$165,000 (2014)

PROGRAM SCOPE

In the past year this grant provided support for one graduate student and partial support for one postdoctoral fellow. One PhD dissertation was published (David Vinyard). His dissertation has produced 5 manuscripts supported by BES, the last of which to be published is listed below. The training of a new first year graduate student, Colin M. Gates, began in January 2014. We report here results from one recently published manuscript and two other manuscripts currently in preparation. Since the inception of this project in June 2010 it has produced five refereed publications, seven national conference presentations, 9 regional or local conference presentations, one PhD dissertation, and one BS honors thesis.

FY 2014 HIGHLIGHTS

- 1) “Engineered Photosystem II Reaction Centers Optimize Photochemistry versus Photoprotection at Different Solar Intensities” D. J. Vinyard, J. Gimpel, G. M. Ananyev, S. P. Mayfield, and G. C. Dismukes. *J. Am. Chem. Soc.* 2014, 136, 4048–4055. [dx.doi.org/10.1021/ja5002967](https://doi.org/10.1021/ja5002967)
- 2) “Quantification and regulation of *in vivo* Photosystem II activity in whole cells controls the rates of production of redox energy and ion gradient energy” G. Ananyev, C. M. Gates and G. C. Dismukes, in preparation.
- 3) “Efficient cycling of the Photosystem II water-oxidizing complex in the thylakoid-less cyanobacterium *Gloeobacter violaceus* PCC 7421” Gennady Ananyev, David Vinyard and G. Charles Dismukes, in preparation.

Analysis of Ethylene-Regulated Growth Networks in *Arabidopsis*

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PROGRAM SCOPE

Seedling growth and its response to changing environmental cues are governed by the collective action of plant hormones. In order to decipher these complex regulatory networks, precise knowledge about each individual plant hormone pathway is essential. The molecular composition of the ethylene signaling pathway is well-studied except for two essential components, EIN6 (ETHYLENE INSENSITIVITY6) and EEN (EIN6 ENHANCER). Recent identification of these genes in our laboratory revealed that both encode chromatin modifying enzymes. Interestingly, only the concomitant loss of both genes leads to a complete ethylene-insensitive phenotype. This insensitivity phenotype of *ein6een* mutant plants is caused by an aberrant localization of certain histone marks leading to a massive transcriptional down-regulation of key signaling components within the ethylene pathway. Thus, we propose a model where EEN and EIN6 cooperatively regulate the accurate deposition of particular histone modifications to control gene expression. A detailed functional characterization of the molecular connection between EIN6 and EEN is carried out in this study to ultimately address the question of how both factors shape the chromatin environment of essential plant growth regulators. This study will also lead to a better

understanding of how plants integrate changing environmental cues into their chromatin environment which is of fundamental importance for plant-based energy research.

FY 2014 HIGHLIGHTS

The *ein6een* double mutant was generated in a fast neutron bombardment mutagenesis screen in the Ler background that aimed to identify new regulatory components of the ethylene signaling pathway. The causal *ein6* mutation is a 7bp deletion in the fifth exon of EIN6. In contrast, the mutation of EEN is caused by a large genomic rearrangement leading to a chimeric gene that consists of EEN and another gene which is located 83kb further upstream. This rearrangement was initially discovered with TAIL-PCR. In addition, we performed structural variation analysis utilizing the Irys platform from BioNano Genomics which independently confirmed and visualized the genomic rearrangement leading to the mutation of EEN. We were also able to generate an *ein6een* mutant in the Col-0 background using T-DNA insertion lines. This new mutant shows almost similar molecular alterations of the chromatin landscape that are apparent in the Ler *ein6een* mutant. Moreover, we performed successful ChIP-seq experiments of EIN6 and EEN revealing a distinct binding pattern. Both factors predominantly bind in gene bodies, in contrast to classical transcription factors which mostly occur in promoter regions. Taken together, our study provides an ideal experimental framework for future studies of chromatin architecture in response to various stresses.

Biochemical and Biophysical Studies of the *E. coli* Aerobic Respiratory Chain

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PROGRAM SCOPE

Proton-coupled electron transfer reactions involving quinones are central to many of the enzymes in biological energy transduction. Understanding how Nature has solved the problem of efficiently converting chemical energy into electrical energy is clearly of importance. We will address aspects of several different, but related questions by examining two different respiratory oxygen reductases: 1) Cytochrome bo_3 from *Escherichia coli*, and 2) cytochrome aa3-600 from *Bacillus subtilis*. Both of these enzymes are members of the A-family of heme-copper oxygen reductases. They are closely related to each other by sequence homology, but they contain different heme prosthetic groups and use different quinols as substrates. Cytochrome bo_3 oxidizes ubiquinol-8 whereas cytochrome aa3-600 utilizes menaquinol-7. These enzymes are proton pumps and couple the redox chemistry of the reduction of O_2 (to water) to the generation of a transmembrane voltage (proton motive force). The mechanism by which these enzymes generate a proton motive force is of primary interest in biological energy transduction. Cytochrome bo_3 is the best characterized of the quinol oxidases and offers practical advantages that facilitate a number of experimental approaches. The protein can be easily prepared from *E. coli* in any amount that is required, from 10 mg to several hundred mg. Importantly, the protein can be genetically manipulated to place either natural or non-natural amino acids at any location. In addition, we have made a series of auxotrophic strains that allow us to selectively label specific amino acids with stable isotopes, which is valuable for different spectroscopic methods.

FY 2014 HIGHLIGHTS

During the past year significant progress was made on several parts of this project.

1) The tyrosine free radical was observed upon reacting hydrogen peroxide with Cytochrome bo_3 . By site directed mutagenesis, this was localized to Y173, located near the active site. This is the equivalent position previously identified in the cytochrome c oxidase from *Paracoccus denitrificans*. We determined that this mutation has no influence on the activity of the enzyme with O_2 , but it does perturb the reaction with hydrogen peroxide. The reaction with O_2 does not generate a tyrosyl radical, consistent with what is observed with other heme-copper oxygen reductases.

2) Although the substitution of a phenylalanine at position 173 (Y173F) eliminates the previously described tyrosyl radical, a new tyrosyl radical is observed. Further site-directed mutagenesis located this mutation at position Y1184 (in subunit II). No tyrosyl radical is observed in the presence of hydrogen peroxide in the double mutant Y173F/Y1184F.

3) Examination of the Y1184F mutant showed that it has remarkable properties. This enzyme when isolated contains a tyrosyl radical with no requirement to add hydrogen peroxide. Upon reduction, the radical vanishes, as expected. The reaction of the reduce enzyme with oxygen, however, generates the tyrosyl radical at residue Y173. It takes minutes for the radical to form to its maximum extent and takes hours for it to dissipate. These properties suggest that the Y1184F mutation may prevent protons from dissociating and re-associating from Y173. Formation of the neutral radical requires removal of a proton, and this proton must be returned upon quenching of the radical. This hypothesis must be tested experimentally. This observation demonstrates that the active site retains a highly oxidized state after the reaction with oxygen, sufficient to oxidize Y173 to a radical.

Studies of Photosynthetic Reaction Centers and Biomimetic Systems

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Funding: \$195,000 (2014)

PROGRAM SCOPE

Computational studies of structure/function relations in photosynthetic proteins aim to elucidate how the physico-chemical constraints of proton coupled electron transfer (PCET) in natural photosynthesis work within the protein and to provide guidelines for the design of artificial photosynthetic systems. The goal is to carry out fundamental studies of proton coupled electron transfer mechanisms in photosynthetic water-splitting in Photosystem II (PSII). The project brings together complementary simulation methods. Gunner (The City College of New York, USA) contributes Monte Carlo techniques for calculations of pK_a s and electrochemical midpoints (Ems). Batista (Yale University, USA) contributes expertise in quantum mechanics and QM/MM methods of PSII and biomimetic oxomanganese complexes. Bruce (Brock University, Canada) provides expertise in large-scale molecular dynamics of photosynthetic reaction centers. Brudvig (Yale University, USA) provides extensive experience in spectroscopic, structural and mechanistic studies of O_2 evolution and photoprotection in PSII. Density Functional Theory (DFT), Quantum Mechanics/Molecular Mechanics (QM/MM), Molecular Dynamics (MD) and Multiconformation Continuum Electrostatics (MCCE) will be applied to study PSII. The overall

aim will be to carry out detailed study of the Mn_4CaO_5 Oxygen Evolving Complex (OEC), a unique redox catalyst that generates oxygen and other redox cofactors in PSII in the context of the surrounding protein. Specific aims include:

- (1) Study of the structural and electronic changes of the Mn_4O_5Ca cluster and ligand cofactors through the S-state cycle.
- (2) Understanding how the surrounding protein influences the OEC redox chemistry and the coupling of oxidation to proton loss in PSII.
- (3) Water is a substrate for the OEC and protons a product. Pathways for water transfer to these active sites will be identified and the energy for transfer evaluated.

FY 2014 HIGHLIGHTS

The combination of experimental information from EXAFS and X-ray diffraction data and DFT QM/MM simulations allows for a significant level of structural refinement of the OEC structure. We have developed a refined QM/MM model of the OEC. A model is developed for the less characterized S_1 state. A hydrogen bonding network, linking the D1-D61 residue to a Mn-bound water molecule, is proposed to facilitate the PCET mechanism. The structural changes of the OEC during the S_1 to S_2 transition show changes in the position of Mn_4 and its coordination environment. Studies of the OEC with Ca^{2+} substituted by Sr^{2+} shows X-ray crystal structures with either Ca^{2+} or Sr^{2+} are most consistent with the S-2 state, with O_4 and O_5 protonated. Ca^{2+} to Sr^{2+} substitution results in elongation of the heterocation bonds and displaces terminal waters that may play a role in water oxidation. A computational model that combines DFT, MD and MC techniques has been used to study the thermodynamics of the OEC S-state cycle in the PSII protein. The model analyzes the entire protein, keeping all acidic and basic residues in equilibrium with the OEC. The S_0 to S_1 includes deprotonation of a μ -oxo bridge, the S_1 to S_2 transition includes deprotonation of terminal water and the S_2 to S_3 transition involves deprotonation of amino acid residue H337. However, within the protein the S_1 to S_2 transition transfers the proton to the adjacent D61 so there is less proton release observed. Water delivery and oxygen removal from the OEC, buried deep within PSII, are needed to facilitate the reaction and minimize reactive oxygen damage. All-atom molecular dynamics simulations of PSII characterized the distribution and permeation of both water and oxygen. Most channels in PSII are permeable to both oxygen and water. However individual channels exhibit different energetic barriers for the two solutes. Selectivity arises from hydrogen bonds between water and channel amino acids, and steric restraints.

Chloroplast Dynamics and Photosynthetic Efficiency

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Funding: \$170,000 (2014)

PROGRAM SCOPE

We are investigating the mechanism by which chloroplasts position themselves to maximize solar energy utilization, to enhance gas exchange, to minimize environmental stress, and to promote efficient exchange of metabolites with other compartments within the plant cell. Chloroplasts move within leaf cells to optimize light levels, moving toward levels of light useful for photosynthesis while moving away

from excess light. Plastids sometimes extend their reach by sending out projections (stromules) that can connect anchor chloroplasts in position within the cell or provide close contacts with plasma membrane, mitochondria, peroxisomes, endoplasmic reticulum, and the nucleus. The intracellular location of chloroplasts in relation to other organelles with which they share biosynthetic pathways, such as peroxisomes and mitochondria in photorespiration, affects metabolite flow. Presently we have little knowledge of the mechanisms of organelle movement and anchoring in specific locations in plant cells. The receptors responsible for detection of light level have been identified, but how the signals ultimately result in chloroplast localization is not understood. We are examining the signal transduction pathway that begins with blue-light and ends with actin-mediated chloroplast movement. Expression of motor proteins and putative signaling intermediates will be disrupted by insertional mutagenesis, virus-induced gene silencing, and/or expression of defective proteins causing dominant negative effects. We will examine the effect of disrupted movement on measures of photosynthetic function. The project will contribute to our understanding of responses of plants to environmental conditions to optimize photosynthesis and minimize photodamage. Information about how plants specify and control chloroplast location will be relevant to attempts to engineer C_4 photosynthesis into C_3 plants as well as to engineering of improved photosynthetic efficiency in C_3 plants.

FY 2014 HIGHLIGHTS

We produced a methods paper describing how to label plastids with fluorescent proteins for observation of their movement and interactions with other subcellular organelles. While carrying out other experiments, we made the unexpected observation that certain types of green fluorescent protein can be photoconverted to a red fluorescent protein. We have submitted a manuscript describing this observation that also demonstrates its use in several different cell types. Using BiMolecular Fluorescence Complementation, we have observed interactions between 14-3-3 proteins and proteins involved in signal transduction for chloroplast avoidance and accumulation. We have found that silencing of a group of 14-3-3 proteins affects light-regulated chloroplast movement. Using mutants altered in their ability to move in response to light, we have observed that the function of chloroplast movement is not merely to avoid photodamage, but also to increase the efficiency of photosynthesis.

Protein Targeting to the Chloroplast Thylakoid Membrane: Structure and Function of a Targeting Complex

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

Biogenesis of thylakoid membrane protein complexes relies on evolutionarily conserved protein sorting/insertion machinery to rout both nuclear and chloroplast encoded thylakoid proteins. Chloroplast signal recognition particle (cpSRP) and its receptor in the chloroplast stroma (cpSRP and cpFtsY, respectively) utilize a chloroplast-specific SRP subunit, cpSRP43, to localize nuclear encoded light-harvesting chlorophyll a/b-binding proteins (LHCPs). LHCPs bind 30-50% of the chlorophyll responsible for photosynthetic light capture in mature chloroplasts. It is well established that cpSRP43

participates in LHC binding to promote formation of an SRP-LHC targeting complex. Our recent studies show that cpSRP43s ability to interact with the LHC targeting substrate, with GTP hydrolyzing targeting components, and with a thylakoid protein insertase, is used to coordinate membrane events that represent the transition from LHC targeting to LHC insertion by the protein insertase Albino3 (Alb3). We hypothesized that cpSRP43-Alb3 interaction serves to coordinate the order and timing of targeting events at the membrane, first triggering structural changes in cpSRP43 that lead to release of LHC from cpSRP to Alb3 followed by cpSRP/cpFtsY mediated GTP hydrolysis, thereby stimulating recycling cpSRP from the thylakoid membrane for additional rounds of targeting. Completion of the proposed biochemical and biophysical studies will be used to establish the order and timing of membrane events needed for LHC targeting to Alb3. The proposed work will also have a general impact on understanding insertase activity of Alb3 homologues required for biogenesis of energy generating complexes in bacteria being used for biofuels production.

FY 2014 HIGHLIGHTS

We show that LHCP is released from cpSRP without the need for GTP hydrolysis; a non-hydrolyzable GTP analogue (GMP-PNP) is sufficient to support LHCP insertion into thylakoids. The use of GMP-PNP to support LHCP targeting/insertion in the absence of cpSRP recycling makes it possible to estimate the number of active Alb3 insertases per chloroplast. We have also found that when Alb3 access is limited, a stable cpSRP-LHCP-cpFtsY complex accumulates at the membrane in the presence of GMP-PNP. Together, these data support a model whereby LHCP remains stably associated with cpSRP at the thylakoid until an Alb3 insertase becomes available. This mechanism would prevent dead-end targeting that stems from premature release of LHCP from cpSRP in the absence of an available insertase. The role of GTP hydrolysis in LHCP localization appears restricted to recycling of cpSRP from its receptor for subsequent rounds of protein targeting. Single molecule Förster Resonance Energy Transfer (smFRET) was employed to understand how cpSRP54 binding to cpSRP43 influences the interdomain structural dynamics of cpSRP43. Careful placement of fluorescent labels at specific sites on cpSRP43 identified several structural features that contribute to cpSRP43 structural dynamics. Upon binding to cpSRP54, the localized flexibility of cpSRP43 is reduced, particularly between the Ank2-Ank4 and CD2-CD3 domains. This flexibility model derived from our experimental FRET data is supported by all-atom and coarse-grained molecular dynamics simulations, which identified 3 main conformations, “closed”, “open” and “extended”. Potential functional implications of these structural dynamics indicate that cpSRP54 binding to cpSRP43 promotes a structure of cpSRP43 that enhances its ability bind LHCP targeting substrates, which was supported by studies that examine the affinity of the cpSRP binding motif in LHCP for cpSRP43.

Targeting, Maturation and Quality Control of Photosynthetic Membrane Proteins

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Funding: \$360,000 (2014-2016)

PROGRAM SCOPE

Thylakoids are internal membrane systems of chloroplasts of photosynthetic eukaryotes and cyanobacteria where light harvesting, electron transport and ATP synthesis occur. Molecular compositions and properties of thylakoids have been elucidated well. By contrast, our understanding of the mechanisms underlying the photosynthetic membrane development and dynamic regulation of photosynthetic activities is far from complete. The overall goal of the BES research project is to address this issue by answering several questions about a thylakoidal protein called plastidic type I signal peptidase 1 (Plsp1). Plsp1 is the major form of thylakoidal processing peptidase (TPP) in the model plant *Arabidopsis*. Protein targeting to the thylakoid lumen requires thylakoid-transfer sequence (TTS) in its N terminus, using ATP-dependent cpSEC pathway or proton motive force-dependent cpTAT pathway for membrane translocation. TPP cleaves off TTS in the lumen. Supported by the DOE grant since 2008, we have made the following discoveries about Plsp1. First, it is essential for proper maintenance of thylakoids thus autotrophic growth of plants. Second, it is located in both the envelope and thylakoid membranes, and its distribution appears to correlate with the development of thylakoids from the envelope. Third, it forms a complex with a protein that plays a role in regulation of cyclic electron flow around the Photosystem I (CEF) although the biological significance of this complex formation is unknown. These findings have generated new questions. In FY2014, we have focused on addressing the following two questions: 1. How does Plsp1 catalyze TTS removal? 2. What is the significance of protein maturation in thylakoids?

FY 2014 HIGHLIGHTS

We have demonstrated catalytic activity of bacterially produced *Arabidopsis* Plsp1 against various TPP substrates including those using cpSEC and cpTAT pathways for transport. We also found that Plsp1 orthologs in angiosperms contain two unique Cys residues located in the lumen. Results of processing assays suggested that these residues were redox active and formation of a disulfide bond between them was necessary for the activity of Plsp1 *in vitro*. Furthermore, Plsp1 in *Arabidopsis* and pea thylakoids migrated faster under non-reducing conditions than under reducing conditions on SDS-PAGE. These results underpin the notion that Plsp1 is a redox-dependent signal peptidase in the thylakoid lumen. We have also gained insights into the mechanism underlying the importance of protein maturation in thylakoid development. In plsp1-null plastids, two TPP substrates that use cpSEC pathway (plastocyanin and PsbO) were shown to be tightly associated with the membrane, while non-mature TPP substrate that uses cpTAT pathway (PsbP) was found in the stroma. The import assay revealed that inhibition of TTS removal did not disrupt cpSEC- and cpTAT-dependent translocation, but prevented release of proteins from the membrane. The non-mature form of plastocyanin was quickly degraded under light, while that of PsbO was found in a 440-kDa complex. The 440-kDa complex was dissociated under reducing conditions. These results indicate that the cpTAT pathway may be disrupted in the plsp1-null mutant, and that there are multiple mechanisms to control unprocessed luminal proteins in thylakoids. Taken together, our data suggest that there may be a mechanism to control the activity of Plsp1, either by redox or association with the CEF regulator, which may be needed to regulate the energy-dependent protein transport. Also, our findings indicate that Plsp1 may be the novel tool to define the mechanism and significance of redox-dependent regulatory pathway in the photosynthetic membrane.

High-Resolution Study of Photochemical and Nonphotochemical Processes in Biological Proteins Assembled with Photosynthetic Pigments

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Funding: \$260,000 (2014-2015)

PROGRAM SCOPE

The research objectives are to study excitonically coupled bacteriochlorophylls (BChls) that are ubiquitous in bacterial photosynthetic complexes. Hole-burning (HB) and delta fluorescence line-narrowing (FLNS) spectroscopies and modeling studies are used to provide additional insight into the excitonic structure, electron-phonon and vibronic couplings, and excitation energy transfer (EET)/electron transfer (ET) processes in: i) various model protein systems; ii) the Zn-reaction center (RC) and its mutants; iii) *Rb. sphaeroides* RC and its mutants; and iv) various FMO complexes, found in anoxygenic green sulfur bacteria. Deeper insight into the origin of hole-burned (HB) spectra will provide a better framework for probing the electronic structure of complex biological systems via HB/FLNS spectroscopies and theoretical calculations. Our approach will provide a more complete picture of the EET/ET processes in various photosynthetic systems.

FY 2014 HIGHLIGHTS

- I. During the FY2014 we showed that various optical spectra (including hole-burned (HB) spectra) for FMO complexes can be properly modeled taking into account uncorrelated excitation energy transfer (EET) between pigments contributing to the lowest-energy states of FMO monomers. A new insight was provided into the nature of the 825 nm exciton band.
Publications: J. Phys. Chem. B 2014, 118 (8), 2032; J. Phys. Chem. Lett. 2014, 5 (8), 1450; and Photosynth. Res. 2014, 120 (3), 323.
- II. We showed that the low-energy Chl a Q_y absorption band in LHCII of PSII have charge-transfer (CT) character as revealed via strong electron-phonon coupling.
Publications: J. Phys. Chem. B 2014, 118 (23), 6086 and PCCP (2014), 16, 20856.
- III. We use both frequency- and time-domain low-temperature spectroscopies to further elucidate the shape and spectral position of singlet minus triplet spectra in the reaction centers of PSII isolated from wild-type *Chlamydomonas (C.) reinhardtii* and spinach. We have shown that the previously observed difference in transient spectra between RCs from *C. reinhardtii* and spinach is not due to the sample origin but due to a partial destabilization of the D1 and D2 polypeptides.
Publications: J. Phys. Chem. B, 2014, dx.doi.org/10.1021/jp510049k and Photosynthesis Research, 2014, submitted.
- IV. Two book chapters are in press:
 - 1) Biophotonics of Photosynthesis, in: Biological and Medical Photonics, Spectroscopy and Microscopy, vol. 4; Ed.: D. Andrews, Publisher Wiley (2014); and
 - 2) Mechanism of Primary Charge Separation in Photosynthetic Reaction Centers, chap. 8 in The Biophysics of Photosynthesis, Springer, Eds. J. Golbeck and A. van der Est (2014). V. Studies of the recombinant water-soluble chlorophyll (Chl) binding proteins (WSCP) from *Lepidium*

virginicum have been completed. This work will be submitted J. Phys. Chem. B. We revealed the presence of uncorrelated EET between two Chl dimers.

Controlling Electron Transfer Pathways in Photosynthetic Reaction Centers

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Funding: \$341,438 (2014)

PROGRAM SCOPE

Photosynthetic reaction centers (RCs) convert light energy into chemical energy in a series of extremely efficient electron transfer reactions that accomplish transmembrane charge separation. RCs have two symmetry-related branches (or sets) of cofactors called A and B that are functionally asymmetric; bacterial RCs use only the A cofactors for light-induced electron transfer. Prior to this project, site-specific mutagenesis efforts had elicited B-branch activity but with only a very low yield of charge separation (~12%). The hypothesis of this collaborative project is that it should be possible to generate an RC that uses the B-side cofactors preferentially and efficiently. The goal is to produce such a transformative RC via the integrated and iterative efforts of the Laible group at Argonne National Laboratory (ANL) and the Kirmaier/Holten group at Washington University in St. Louis (WU). Our primary experimental vehicle is the RC from the purple photosynthetic bacterium *Rhodobacter (R.) capsulatus*. RC mutagenesis and protein purification are conducted at ANL and mutant RCs are screened via a high-throughput time-resolved spectroscopic assay at WU. Promising mutants (“hits”) re-enter the pipeline for subsequent rounds of 1) mutation and screening (ANL and WU) and/or 2) natural selection seeking photosynthetic growth that uses the B-side cofactors only (ANL) and/or 3) further characterization of the rates and yields of RC electron transfer steps via ultrafast spectroscopy (WU). The ultimate goal is to discover and understand the architectural and energetic factors that will transform the B-side cofactors from a normally non-functional state into one of high functionality. The principles realized will be broadly applicable, such as aiding design of biomimetic systems that are competent in light-induced ET and that provide a long-lived charge-separated state that can be an energy source for downstream energy conversion and storage.

FY 2014 HIGHLIGHTS

Both technical and scientific advances were made in 2014. Regarding the former, efficiencies of RC mutant construction and RC protein purification processes at ANL continued to be improved via streamlining or eliminating some steps while preserving or even increasing the quality of the output. At WU, the sensitivity and signal-to-noise ratio of the millisecond-to-seconds high-throughput screening assay also continued to be optimized such that assays can now be performed with samples of about one-tenth the concentration used two years ago. Some highlights of our scientific findings are as follows:

- (1) About 100 new mutants were generated and screened with many displaying enhanced overall yield of B-side charge separation.

- (2) Ultrafast transient absorption studies on select mutants detailed the rates and yields of each of the step-wise B-branch electron transfer reactions. These analyses revealed specific mutations that in some cases improve the initial, primary photochemistry (electron transfer from the photoexcited primary donor to the intermediate electron carrier) or in other cases improve the secondary stage of the photochemistry (electron transfer from the intermediate to the terminal quinone).
- (3) Studies on mutant RCs from *R. sphaeroides* that complement work on *R. capsulatus* were conducted and revealed differential effects (for the same mutation) that may be exploited.
- (4) Efforts to use natural selection methods to discover mutations that result in photosynthetic competence from use of only the B-side cofactors are underway and showing promise.

Collectively, this work demonstrated significant progress toward understanding and engineering an efficient B-branch electron transfer pathway in the bacterial photosynthetic RC. Such knowledge is applicable to the design of artificial systems for solar energy conversion using inspiration from the native photosynthetic systems.

The Energy Budget of Steady State Photosynthesis

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 Funding: \$230,000 (2014)

PROGRAM SCOPE

The work focuses on how photosynthesis balances its energy budget, matching the output of energy in NADPH and ATP to precisely meet biochemical demands, which is critical for efficient, robust photosynthesis. We are currently focusing on the mechanism and modes of regulation of cyclic electron transfer around photosystem I (CEF), which is important in balancing ATP/NADPH output.

FY 2014 HIGHLIGHTS

The work focuses on how photosynthesis balances its energy budget, matching the output of energy in NADPH and ATP to precisely meet biochemical demands, which is critical for efficient, robust photosynthesis. We have made important breakthroughs on all proposed aims, resulting over the past year in the publication of three papers citing support from this grant (1-3), two manuscripts are accepted for publication and are In Press (4, 5) and four additional manuscripts are in revisions. We have also made progress on characterization of (and appropriate controls for) CEF mutants (hcef4, hcef5 and hcef6). We are accordingly nearly ready to publish on two of these mutants. Most excitingly, our very recent work shows that the chloroplast NDH complex 1) is a proton pump; 2) the proton pumping capacity of NDH allows it to be driven 'in reverse' under conditions of high pmf; 3) NDH affects the ion permeability of the thylakoids, perhaps because it acts as a H⁺/Na⁺ antiporter as proposed for the bacterial and mitochondrial homologues (Complex I); 4) the NDH complex can be driven in reverse, oxidizing plastoquinol and reducing stromal electron carriers. Based on these results, we propose that the NDH complex may act as a regulatory system that senses the balance of energy stored in the pmf, redox carriers and ATP.

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Photoreceptor Regulation and Optimization of Energy Harvesting in *Nostoc punctiforme*

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 Funding: \$739,000 (2014)

PROGRAM SCOPE

Sustainable bioenergy production relies on the ability of photosynthetic organisms to use solar power to convert atmospheric carbon dioxide into organic fuels such as biodiesel. While plants effectively harvest solar energy and accumulate biomass, plant growth for energy production requires extensive use of nitrogen fertilizers and competes with food production for arable land. Algal and bacterial photosynthesis provide powerful alternatives. Cyanobacteria are among the most versatile photosynthetic organisms known, frequently fixing their own nitrogen and readily growing in liquid culture or in swamplands. Nitrogen fixation produces hydrogen gas as a byproduct, and hydrogen production allows energy to be made without converting biomass into usable fuel. Our work addresses both basic science and applied science of these organisms, with a long-term goal of engineering cyanobacteria as a sustainable bioenergy source. Such engineering requires the development of inducible gene regulatory systems, allowing researchers or engineers to manipulate the metabolism of the organism for optimal energy production. Using photosensory systems for this purpose permits control over the level of induction (by varying the quantity and quality of light) and can avoid problems associated with other artificially controlled inducers, such as heat-shock systems or expensive synthetic chemicals. This project seeks to characterize all bilin-based photosensors in the cyanobacterium *Nostoc punctiforme*, to understand the molecular basis of their light sensing selectivity and signaling activity, and to apply them in synthetic photosensory circuits to regulate gene expression.

FY 2014 HIGHLIGHTS

Following completion of our survey of the phytochrome superfamily of bilin-based light sensors in *N. punctiforme*, we initiated detailed investigations of targeted subfamilies with distinct light-sensing selectivities. We characterized a widespread tuning mechanism used by many of these photosensors that relies on conserved phenylalanine residues. This work aids both engineering of new photocycles and prediction of cyanobacterial photobiology from genome sequence. Time resolved photodynamics of the cyanobacterial phytochrome Cph1 and two cyanobacteriochromes, NpF2164g3 and RcaE, on the

femtosecond to nanosecond timescale revealed heterogeneity to be the rule rather than the exception with these photosensors. Such heterogeneity accounts for variable quantum efficiency and photoproduct diversity observed within individual subfamilies. Room temperature NMR studies of NpF2164g3 in both photostates identified a conserved light-induced structural change, permitting construction of an explicit, testable model for signal-propagation by cyanobacteriochromes.

Elucidating the Principles that Control Proton-Coupled Electron Transfer Reaction in the Photosynthetic Protein, Photosystem II. A Model for Design of Bio-Inspired Photocatalytic Water-splitting

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Funding: \$165,000 (2014)

PROGRAM SCOPE

The solar water-splitting protein, photosystem II (PSII), catalyzes one of the most energetically demanding reactions in nature by using light energy to drive a catalyst capable of oxidizing water. Proton-coupled electron transfer (PCET) reactions, which are exquisitely tuned by smart protein matrix effects, are central to the water-splitting chemistry of PSII and elucidating the water-splitting chemistry of PSII is of major importance in designing bio-inspired catalytic systems for solar fuels production. Proton motion coupled to electron transfer is the basic mechanism of biological energy conversion. However, a major challenge is to develop methods to directly probe PCET processes to understand the structural requirements for minimizing the energetic penalty for multiple charge transfers. The overall objective of this project is to understand the tuning and regulation of the PCET reactions of PSII. The specific goals of this research are: a) To understand the primary factors that influence the tuning of PCET processes in the oxygen-evolving complex (OEC) and b) to elucidate the role of “smart” matrix effects of the protein in tuning the charge-transfer sites of PSII. In order to achieve these goals, we are (i) determining the structure of the S-state intermediates of the OEC in the water oxidation reaction, (b) using metal-ion substitution in conjunction with pulsed EPR spectroscopy to determine the role of the Ca^{2+} ion in the water oxidation reaction, (c) elucidating the mechanism of PCET at the redox-active tyrosine residues, YZ and YD and (d) developing methods to probe protein-cofactor interactions that govern the functional specificity of the quinone cofactors, Q_A and Q_B , of PSII.

FY 2014 HIGHLIGHTS

We had previously detailed the structure and location of the substrate water molecules that are directly coordinated to the Mn_4Ca -oxo cluster in the S_2 state of Ca^{2+} -substituted PSII. In a very exciting development, we have unambiguously identified the substrate water molecules that are coordinated to the catalytic Mn_4Sr -oxo cluster in the S_2 state of Sr^{2+} -substituted PSII. This provides, for the first time, a direct window into the role of Ca^{2+} in the solar water oxidation reaction of PSII. The Sr^{2+} -substituted PSII was prepared in collaboration with Prof. Shen (Okayama University). Previously, we had also demonstrated the presence of three nitrogen atoms that are magnetically interacting with the Mn_4Ca -oxo cluster in the S_2 state of PSII and we had confirmed the assignment of these hyperfine interactions in dimanganese di- μ -oxo model complexes. Recently, we have utilized two-dimensional ^1H , ^2H and ^{14}N hyperfine sublevel correlation (HYSCORE) spectroscopy to characterize the structure of the active site of

super-oxidized (Mn(III)Mn(IV)) manganese catalase. The (Mn(III)Mn(IV)) form of manganese catalase is an excellent proteinaceous model of the Mn₄Ca-oxo cluster of PSII. The super-oxidized (Mn(III)Mn(IV)) manganese catalase was prepared in collaboration with Prof. Whittaker (Oregon Health & Science University). In addition, we have detailed the individual steps of the highly efficient PCET reactions mediated by the redox-active tyrosine residues of PSII. This study provides a blueprint for biological PCET reactions in solar energy conversion. Currently, we are conducting multi-dimensional pulsed EPR spectroscopy studies of genetic variants with mutations in the primary quinone, Q_A, binding pocket of PSII. This provides insight on the factors that tune and control the function of the quinone electron acceptors in PSII. The genetic variants of PSII have been prepared in collaboration with Prof. Debus (UC, Riverside).

Membrane Bioenergetics of Salt Tolerant Organisms

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Funding: \$75,000 (2014)

PROGRAM SCOPE

With the discovery of the globally significant abundance of retinal-based proton pumps, we focus on generalizing and extending the bacteriorhodopsin paradigm. There is abundant evidence now that the lessons to be learned from the rhodopsins are much broader than previously thought. Our earlier finding that in the *Exiguobacterium* rhodopsin a lysine, instead of an acidic group, is the proton donor to the retinal Schiff base raises the question whether the source of the proton is the lysine NH³⁺ itself or an associated water molecule (or water network). We will explore these alternatives with IR spectroscopy and mutagenesis of the region around the lysine. Increased hydration at a late step of the transport cycle, as in bacteriorhodopsin, would account for the fact that although the donor is unprotonated in the initial state, it becomes transiently protonated from the bulk before it reprotonates the Schiff base. In the *Exiguobacterium* rhodopsin at about the time the Schiff base becomes deprotonated, a proton is released before a second proton is taken up. We will study the origin of this proton, and whether it is a consequence of a pK_a change of some buried group in response to a protein conformational shift. It is intriguing that the conformational change at the time this proton is released should be on the extracellular rather than the cytoplasmic side, the latter having been more thoroughly investigated in the rhodopsins. *Hymenobacter* rhodopsin is novel and an unusual proton pump with the conventional carboxyl proton acceptor and donor replaced by asparagine and glutamine. An alternative acceptor might be an aspartate residue one helical turn removed from its expected location. It is unclear what the donor is. We will describe how this unusual pump functions. Unexpectedly, in the presence of Na⁺ this rhodopsin transports Na⁺ instead of protons. We will identify the site(s) where the switch between the two kinds of transport functions occurs.

FY 2014 HIGHLIGHTS

1. Nature of the proton donor in *Exiguobacterium sibiricum* rhodopsin (ESR) and mechanism of Schiff base reprotonation. Uniquely, ESR contains Lys instead of the conventional acidic group in the position of the proton donor to the retinal Schiff base. In the proposal, we asked: "...what will

happen if a carboxylic residue replaces Lys96, as in all other conventional proton pumps? Will it be able to perform as internal donor?" We have now obtained an affirmative answer to this question. In the wild type ESR reprotonation of the Schiff base (the decay of M intermediate, followed as the decrease of absorbance 410 nm) occurs in ca. 1 ms. In the K96E mutant reprotonation occurs with a rate only slightly slower than in the wild type, and in the K96D/A47T it is even faster than in wild type (0.7 ms vs. 1 ms). This indicates that a carboxylic residue in place of Lys96 will efficiently facilitate proton transfer from the bulk to the Schiff base. Other ionizable residues in place of Lys96 (Arg or His) were not able to do this.

- II. Proton release mechanisms in ESR: role of carboxylic and other groups. We examined the source of the proton that is released to the extracellular surface before uptake at the cytoplasmic surface. We mutated all carboxylic residues in ESR, found that only mutation of Glu214 in the extracellular domain eliminates fast proton release. It also affects the pK_a of the blue shift of absorption spectrum which was attributed to deprotonation of His. Mutation of Glu214 to Asn facilitates also rapid Schiff base deprotonation. These results suggest that a strong hydrogen bonding network at the Schiff base regulates Schiff base deprotonation and proton release.
- III. Proton transport in *Hymenobacter roseosalivarius* rhodopsin (HRR) with changed or absent internal proton acceptor and donor. We identified Asp102 as the principal counterion that interacts strongly with the Schiff base.

Immunophilins in the Assembly and Maintenance of Photosynthetic Electron Transport Chain in *Arabidopsis*

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Funding: \$75,000 (2014)

PROGRAM SCOPE

The proposed project is to understand the function of immunophilins in the assembly and maintenance of photosynthetic complexes in *Arabidopsis*. Our studies have identified critical functions for several immunophilins in the biogenesis and maintenance of photosynthetic electron transport chain. Among the four protein-based electron carriers in the thylakoid, three (PSII, Cyt bf, and PC) have been shown to require immunophilins for their assembly. Furthermore, function of 2/3 of the 16 immunophilins in the thylakoid lumen is yet to be assigned. It becomes increasingly apparent that immunophilins in the thylakoid may constitute an "assembly line" for photosynthetic machines. Our goal is to establish this emerging concept by systematically dissecting the functions of all immunophilins in the context of photosynthetic light reaction. The specific objectives for this funding period will focus on mechanistic analysis of two thylakoid lumen immunophilins, FKBP20-2 and CYP38, which are involved in the assembly and maintenance of PSII. At the same time, we will expand our effort into the functional analysis of another immunophilin (CYP37) that is required for the accumulation of Cyt b6f complex. The work on FKBP16-2 in PC assembly briefly described above (details in attached preprint) has been completed at a mechanistic level. No immediate work is planned on FKBP16-2 in this proposal because the further work on this immunophilin will heavily rely on chemistry and structural tools beyond our direct expertise. Collaborative research is currently being explored.

FY 2014 HIGHLIGHTS

We have identified and characterized the function of a new player in the thylakoid lumen that interact with immunophilins and that plays a critical role in plant growth under variable light intensities. The function of this protein is independent of the formation of PSII supercomplexes and state transition. This finding has been published in PNAS at the beginning of 2015.

Molecular Genetic Dissection of Chloroplast Iron Homeostasis

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PROGRAM SCOPE

Iron nutrition limits life because of poor bioavailability. The long-term goal of this project is to understand iron-nutrition dependent programming of chloroplast and mitochondrial metabolism in photosynthetic eukaryotes. Recent studies have contributed to the appreciation that photosynthetic metabolism and output from the photosynthetic apparatus is dependent on resource (CO₂, light, mineral nutrients) availability and is also tightly connected to respiratory function. *Chlamydomonas reinhardtii* has served as a premier reference organism for discovering and understanding the regulatory circuits that connect carbon source, photon flux density and inorganic nutrients to the operation of the light and dark reactions of photosynthesis. In this context, the specific aims for the new project period are,

1. To compare the transcriptomes of iron-replete, -deficient and -limited cells during the transition from photoautotrophic to photoheterotrophic growth with the goal of identifying the factors involved in iron salvage from the photosynthetic apparatus and iron delivery to the respiratory chain and better understanding of the connection between C metabolism and Fe nutrition.
2. To describe the elemental profile of the proteomes of cells grown in iron-luxury vs. iron-economy mode to compare and document the distribution of iron.
3. To determine the function of CGLD27 and FEK1 by localizing them and determining the molecular phenotype of *cgld27* and *fek1 Arabidopsis* plants or *Chlamydomonas* strains with respect to iron nutrition.

FY 2014 HIGHLIGHTS

Aim 1. In the last project period, replicate photoautotrophic cultures were grown with iron supplied at 0.25, 1 and 20 μM, representing the limited, deficient and replete states, respectively. Acetate was added to cultures in log phase following which they were monitored for biomass and chlorophyll and sampled for isolation of RNA immediately after addition (0 h) or 1, 2, 4, 6, 8, 12 and 24 h later. Physiological measurements indicate that the iron-limited culture behaves distinctly different from the iron-deficient and -replete cultures with respect to growth and Chl content, supporting our previous findings of a different metabolic state. The reduction in Chl content to 50% is timed precisely between 4 to 6 h. This reduction cannot be explained by cell division because the cells do not divide until many hours later. We suspect that the program to degrade the photosynthetic apparatus is initiated during this window.

Aim 2. We had proposed to use elemental profiling of the proteome to ascertain the location of intracellular Fe. In the iron-excess situation, this would address the question of where iron is stored, since ferritin abundance actually decreases in the overload situation. In the case of deficiency, the profile would reveal other iron-containing proteins that are either prioritized or dispensable. The amount of iron that is associated with ferritin increases as cells transition from iron-limited to iron-deficient to iron-replete, but once the cells are iron-replete, the ferritin associated iron remains constant even though intracellular iron increases nearly 5-fold. The abundance of the polypeptide actually decreases 10-fold in iron-excess vs. iron-limited cells, which translates to over 100-fold increase in the iron content of the ferritin. Preliminary data suggest that the non-ferritin associated iron is in compartments that also contain calcium.

Enhancement of Photoassimilate Utilization by Manipulation of ADP-glucose Pyrophosphorylase and Phosphorylase

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Funding: \$90,000 (2014)

PROGRAM SCOPE

ADPglucose pyrophosphorylase (AGPase) and the plastidial starch phosphorylase1 (Pho1) are two regulatory enzymes whose catalytic activities are essential for starch granule synthesis. Conversion of the pre-starch granule to the mature form is dependent on AGPase, which produces ADPglucose, the substrate used by starch synthases. We had earlier demonstrated that the AGPase catalyzed reaction limits the amount of starch accumulation in developing rice seeds and that carbon flux into rice seed starch can be increased by expression of a cytoplasmic-localized, up-regulated bacterial AGPase enzyme form. Results of subsequent physiological and metabolite studies showed that the AGPase reaction is no longer limiting in the AGPase transgenic rice lines and that now one or more downstream processes prevent further increases in starch biosynthesis. A second phase of this project examines Pho1, the enzyme required during the initial phase of pre-starch granule formation and its maturation to a starch granule. Although Pho1 catalyzes a reversible reaction, our DoE supported studies clearly demonstrated that the kinetic properties of this enzyme strongly favor synthesis of starch and that these catalytic properties are independent of the L80 peptide, a structural domain that is absent in phosphorylases from other organisms. Current efforts are directed at elucidating the role of the L80 peptide in regulating Pho1. Overall, results from these biochemical and physiological studies will increase our fundamental understanding on how these important starch regulatory enzymes operate at the molecular level and *in planta*, which will collectively aid in efforts to increase the utilization of higher plants as a renewable source of energy.

FY 2014 HIGHLIGHTS

1. A study on the regulation of the rice AGPase was completed and published. Redox control of the partially purified native enzyme not only affected affinity to the activator 3-PGA but also k_{cat} whereas redox regulation only affected 3-PGA affinity of the recombinant enzyme.

2. The interactions of substrates to heterotetrameric (SWTLWT) and homotetrameric (L302N and SWT) forms of ADP-glucose pyrophosphorylase were investigated using isothermal titration calorimetry. Our results clearly demonstrated that wildtype SWTLWT possesses two distinct types of ATP binding sites with significantly increased affinity compared to L302N and SWT homotetrameric enzymes. Interestingly, binding to the other substrate, glucose-1-phosphate, was not observed suggesting that AGPase may not have a defined binding site for this sugar-phosphate.
3. RNAseq studies showed that RNAs for several starch biosynthetic enzymes were elevated or depressed several-fold in the starch over-producing transgenic rice line modified for elevated AGPase activity. The most conspicuous transcriptome change (4-12 fold increase) was for a starch binding domain protein, which has never been isolated and biochemically characterized. These changes at the RNA level were also evident at the protein level. This starch binding domain protein may limit starch granule synthesis by competing against the binding of starch biosynthetic enzymes to starch chains.
4. The interaction of Pho1 with disproportionating enzyme (Dpe1) to form a multi-enzyme complex was verified by using Dpe1 as bait, which readily captured native Pho1 from seed extracts.
5. Transgenic rice lines of the Pho1 mutant BMF136 expressing intact Pho1 and Pho1 Δ L80 genes were generated. Interestingly, the Pho1 Δ L80 transgenic lines grew faster and produced larger grains than transgenic lines expressing wildtype Pho1. These observations suggest that the L80 peptide is a negative regulatory structural domain of Pho1.

Control of Chloroplast Morphology in Plants: Mechanisms and Physiological Significance

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PROGRAM SCOPE

The proliferation of chloroplasts in leaf mesophyll cells through the process of division increases chloroplast numbers and compartment size during leaf growth and development, and is therefore essential for achieving maximum photosynthetic productivity. A striking feature of the division process is that it is restricted to the middle of the chloroplast, producing a large population of small organelles of similar size and shape. The first contractile component of the chloroplast division machinery to assemble is the stromal FtsZ ring (Z ring), which determines the positioning of other contractile components of the division complex. The tight spatial regulation of division-site placement is regulated by a complex system of proteins that together inhibit Z-ring assembly everywhere but at the chloroplast midpoint. The proposed research is aimed at furthering our understanding of the mechanisms restricting Z-ring formation to the mid-plastid, exploring the physiological significance of chloroplast size and shape for photosynthetic performance, and exploiting genetic variation in *Arabidopsis* to identify genetic loci potentially involved in the control of chloroplast size, number and total compartment size.

FY 2014 HIGHLIGHTS

ARC3 and PARC6 contribute to regulating Z-ring positioning. We showed that ARC3 is a direct FtsZ assembly inhibitor, and previous data have suggested that PARC6 also inhibits Z-ring assembly. To

confirm this, we generated *Arabidopsis* plants overexpressing PARC6, which exhibit enlarged chloroplasts indicative of impaired division. Immunofluorescence staining in T1 transgenics showed that FtsZ localizes to small punctae instead of rings. To test our hypothesis that the inhibitory effect of PARC6 on Z-ring assembly results from its interaction with ARC3, we are generating plants that overexpress PARC6 in *arc3* mutants. We predict that multiple FtsZ rings or filaments will be observed in these plants. To explore the relationships between chloroplast morphology, chloroplast movement and photosynthesis, we collaborated with David Kramer to develop a platform for imaging chloroplast movements and chlorophyll fluorescence on whole plants in white light using dual CCD cameras. Reflectance of pulsed red light from leaf surfaces measures chloroplast movement. Image data are integrated over all exposed leaves. With this platform we measured chloroplast movement and photosynthetic responses to fluctuating light in *Arabidopsis arc6* and two *ftsZ* mutants, which bear 1-2 giant chloroplasts in their mesophyll cells, and compared their responses to those of phot mutants, which exhibit impaired movement but normal chloroplast morphologies. The data indicated reduced movement in all mutants, confirmed by confocal microscopy, and showed that reflectance accurately reports chloroplast movements. Large-chloroplast mutants showed lower PSII efficiency and recovery from high-light stress than wild type. These responses differed from those of phot mutants, suggesting that the altered photosynthetic responses in the *arc6* and *ftsZ* mutants are not due solely to their impaired movement responses. Other photosynthetic parameters (NPQ and photoinhibition) are being analyzed in these mutants.

Redox Factors in the Thylakoid Lumen for Protection and Repair of the Photosynthetic Apparatus

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PROGRAM SCOPE

Cyanobacteria are the largest and most diverse group of oxygenic photosynthetic prokaryotes that play major roles in bioenergy production and carbon sequestration on our planet. They are also the progenitors of chloroplasts in plants and eukaryotic algae. In these organisms, production of oxygen from water by the Photosystem II (PSII) pigment protein complex on the luminal side of the thylakoid membrane requires a very strong oxidant, whereas the electron transfer reactions in the Photosystem I (PSI) complex on the cytoplasmic side of the same membrane generates a strong reductant. The simultaneous presence of highly oxidizing as well as reducing environments during the normal photosynthetic electron transfer reactions in cyanobacteria inevitably leads to the production of reactive oxygen species (ROS) that can potentially damage the photosynthetic apparatus. To face this challenge, cyanobacteria have developed multiple protection and repair pathways. The central objective of this project is to determine the mechanisms of thylakoid lumen localized redox proteins in photoprotection and repair of the photosynthetic apparatus. During the current funding period of this project, there are four specific aims: (1) To develop a simple and rapid method for the isolation of functionally competent thylakoid membranes from cyanobacteria, followed by analysis of the proteome of the thylakoid lumen; (2) To generate comprehensive maps of the thylakoid and plasma membrane proteomes of cyanobacteria; (3) To dissect the Redox Proteome of cyanobacterial thylakoid lumen, and (4) To investigate the role of a thylakoid lumen-localized thioredoxin-like protein as a critical regulator of

photosystem stoichiometry. These comprehensive studies are expected to broaden our understanding of the important roles of the thylakoid lumen in the protection and repair of the photosynthetic apparatus.

FY 2014 HIGHLIGHTS

During this year, we investigated the global redox proteome of the cyanobacterium *Synechocystis* 6803, and developed a proteome-wide quantitative site-specific profile of *in vivo* dynamics of thiol oxidation in this organism. In photosynthetic organisms, reversible protein thiol oxidation is an essential regulatory mechanism for many physiological processes. During the current project period, we aimed at examining the redox states of all protein thiols in a cyanobacterial cell in the presence or absence of photosynthetic electron transport activity. Toward this goal, we first developed a novel global proteomic approach for selective enrichment of oxidized thiols with quantitative isobaric labeling to determine the extent of oxidation of individual thiols, as well as the redox dynamics of the thiol proteome under different conditions that modulate photosynthetic electron transport activities in the thylakoid membranes of *Synechocystis* 6803 cells. The proteomics results exhibited consistent increases in the levels of cysteine thiol oxidation in the dark compared to the light condition. In total, changes in Cys oxidation status were observed in ~2600 peptides from ~1000 proteins, implying broad light-dependent redox regulation in this organism. In particular, the level of thiol oxidation for many known redox proteins such as thioredoxin, PSI and PSII reaction center proteins, and various oxidoreductases were significantly modulated. These results are consistent with earlier findings that specific electron carriers in the photosynthetic electron transport chain are increasingly oxidized during dark incubation than under light, and that disruption of the electron flow alters the redox state of the electron carriers. Interestingly, the identified redox-sensitive proteins are broadly involved in various biological processes, including photosynthesis, carbon fixation, amino acid biosynthesis, glycolysis and respiration.

Biochemical Integration of Metabolic Networks Critical for Energy Transformation in *Chlamydomonas reinhardtii*

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PROGRAM SCOPE

We are exploring *Chlamydomonas* energetics, with an emphasis on proteins required in dark metabolism, and identifying dark-specific electron carriers, supramolecular metabolic complexes, alternative electron transport pathways, and how these pathways interface with photosynthetic processes, which dominate during the day. Basic and specific questions being addressed are:

Why is an acetate kinase mutant (*ack1*) unable to grow in the dark?;

What targets of ferredoxin 5 (FDX5) dependent reduction are absolutely required for dark growth?

Why is the bifunctional alcohol dehydrogenase (ADH1) the dominant enzyme for reoxidation of electron carriers when O₂ is unavailable, and how is ADH1 activity regulated with respect to the many other enzymes that also use acetyl-CoA as a substrate?;

What is the role of the oxyhydrogen reaction in nature and how are electrons from H₂ captured in the dark and used to generate ATP and reductant?; and

How do conditions associated with oxyhydrogen function (dark, H₂, low O₂) alter pigmentation and pathways of electron flow?

One of the largest undertakings that we have initiated involves elucidating interactions among proteins associated with major hubs in dark and fermentation metabolism. Metabolite 'guiding' likely involves the linking of specific enzymes for the efficient trafficking of metabolites as a consequence of multi-protein, mega-complex formation. The key enzymes used for the analyses of protein complex formation are ADH1, the [FeFe]-hydrogenases (HYDA1/2) and PAT/ACK (chloroplast and mitochondrial), as well as pyruvate ferredoxin oxidoreductase (PFR1) and pyruvate formate lyase (PFL). The linking of enzyme activities through physical interactions might not only lead to efficient channeling of metabolites, but also potentially introduce rapid and effective mechanisms for fine tuning the activities of individual components through the binding of reactants and products.

FY 2014 HIGHLIGHTS

Key findings include characterizing the roles of chloroplast and mitochondrion acetate kinase (ACK) and phosphate acetyltransferase (PAT) in fermentation and dark oxic metabolism, the requirement for a specific ferredoxin (FDX) for anabolic electron transfer and growth in the dark, the further characterization of mutants null for both hydrogenases (HYDA1 and HYDA2), and insights into the operation of the oxyhydrogen reaction in the generation of reductant and ATP from H₂. Some of our novel, and surprising results include: (i) chloroplast localized ACK1 is critical for growing *Chlamydomonas* in the dark with acetate as a fixed carbon source (likely required for entry of acetate into plastid metabolism); (ii) FDX5 is critical for growth of *Chlamydomonas* in the dark, and is also important for maintaining the proper stoichiometry of galactolipids in thylakoid membranes, which likely reflects its role in donating electrons to fatty acid desaturases; (iii) the oxyhydrogen reaction (utilization of H₂ for the generation of ATP and reductant in the dark concomitant with O₂/CO₂ uptake) can restore dark growth of the *fdx5* mutant, potentially because the H₂ can be used to reduce FDX1 (FDX1 would not be readily reduced in the dark by NADH, unlike FDX5); (iv) oxyhydrogen reaction conditions cause modifications in cell pigmentation (carotenoid composition appears to change), and the cells potentially experience alterations in the architecture of the photosynthetic apparatus. Overall, our results suggest the need to generate more basic information concerning functional and regulatory rules controlling metabolism in both the light and dark if we are to understand the energetics and ecology of algae and plants, and ultimately use our understanding of basic metabolism for generating bio-products from photosynthetic organisms.

The Type I Homodimeric Reaction Center in *Heliobacterium modesticaldium*

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Funding: \$325,000 (2014)

PROGRAM SCOPE

Our understanding of the homodimeric Type I (Fe/S-cluster) reaction centers is primitive, partly due to the difficulties of working with the anaerobic organisms that use them. In the case of the heliobacterial reaction center (HbRC), the facile conversion of the BChl g pigments to a Chl a-like molecule in the presence of O₂ necessitates that all work be done in anoxic conditions. We have found that the HbRC is very different from Photosystem I in the past funding period. In this project, our goals are to:

- (1) Investigate the properties of the F_x cluster. We have evidence that the PshBI and PshBII polypeptides serve as electron acceptors, rather than as subunits of the HbRC, implying that the F_x cluster is the biologically relevant terminal electron acceptor. We will determine the midpoint potential of F_x and we will establish if the protein makes use of the [4Fe-4S]²⁺/ [4Fe-4S]¹⁺ and/or [4Fe-4S]¹⁺/ [4Fe-4S]⁰ redox couple(s).
- (2) Study soluble electron acceptor proteins. We will determine the midpoint potentials of the FA and FB clusters in PshBI and PshBII and we will measure transcript and protein levels of PshBI and PshBII. We will also determine whether the dicluster ferredoxins HM1_0860 and MM1_2505 and the bacterial [FeFe]-hydrogenase can accept electrons directly from F_x.
- (3) Uncover the physiological role of the quinone. We will continue to seek a role for the quinone as an intermediate cofactor but we are also expanding our search to include a possible role as an alternative terminal electron acceptor.
- (4) Develop a genetic transformation system for *H. modesticaldum*. We will develop of a system to integrate DNA into the genome of *H. modesticaldum*, which would open the door for new experiments.
- (5) Solve the 3-dimensional structures of the HbRC. We will crystallize the PshA2 homodimer and determine its structure by X-ray crystallography.

FY 2014 HIGHLIGHTS

We have made advances in all of the sub-projects listed in our Scope:

- (1) We have determined the midpoint potential of the interpolypeptide F_x [4Fe-4S] cluster to be -500 mV (vs. SHE), which is much more positive than the F_x cluster in Photosystem I (PSI). Also unlike PSI, the F_x cluster appears to be the terminal acceptor, and therefore donor to all RC acceptors, since the PshB polypeptide(s) no longer appears to be a subunit.
- (2) We have determined the midpoint potentials of the [4Fe-4S] clusters in the PshBI and PshBII polypeptides to be in the -450 to -500 mV range, providing a small driving force for them to serve as acceptors. The ferredoxin encoded by the HM1_2505 gene is in the same range. We have measured transcript levels of all of the ferredoxins using next-generation sequencing, and found that PshBI and PshBII are the most highly expressed.
- (3) We have confirmed that the embedded menaquinone (MQ) does not serve as an intermediate cofactor: HbRC having or lacking MQ behave identically in ultra-fast pump-probe experiments for electron transfer from P800 (ultimate donor) to F_x. Illumination of membranes results in reduction of the pool MQ to MQH₂ when soluble electron acceptors are lacking, and that there appears to be a cycle operating between the HbRC and cytochrome bc complex. This would make the HbRC intermediate in function between PSI and the type II RCs.
- (4) We are developing a system to integrate DNA into the genome of *H. modesticaldum*. We have cloned four DNA methyltransferases associated with restriction endonucleases in the genome and constructed an artificial operon with them in *E. coli* to methylate plasmids by the heliobacterial enzyme before conjugation into *H. modesticaldum*.

- (5) We have crystallized the PshA2 homodimer in several different forms. By the end of the fiscal period, we had obtained diffraction to $\sim 5.5\text{-\AA}$ resolution, which is the best we have ever obtained. Efforts continue to improve resolution.

Revealing Excitonic Structure and Charge Transfer in Photosynthetic Proteins by Time-resolved Circular Dichroism Spectroscopy

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Funding: \$330,000 (2014-2015)

PROGRAM SCOPE

The goal of the project is to shed light on intrinsic properties of photosynthetic proteins that are used in nature to capture the energy of sunlight and convert it to other forms of energy such as electronic current. Prior to September 2014, the main goal of the project was to evaluate novel unconventional photoprotection mechanisms in photosynthetic pigment-protein complexes, in particular the formation of triplet excitons in closely coupled systems, and possible tuning of the electronic properties of the pigments by the protein environment. Several artificial and native systems have been studied: chlorosomes, Fenna Matthews Olson (FMO) complex and artificial aggregates of pigments. Beginning from September 2014, the project is focused on the development and application of new experimental technique - the optical time-resolved circular dichroism (TRCD) spectroscopy - and its application to investigate the energy transfer/conversion mechanisms in the Fenna Matthews Olson (FMO) light-harvesting complex and photosystem I reaction center (PS I RC). The FMO complex contains 24 closely spaced bacteriochlorophylls (BChls), which leads to strong interaction between them and results in highly delocalized optical excitations (excitons). Combining optical dichroism spectra with femtosecond and nanosecond time resolution will allow us to follow both singlet exciton energy transfer and triplet excitation transfer in real time via their CD signatures, assign the individual pigment properties and test the power and capability of the TRCD. PS I is a key photosynthetic protein complex shared by all green plants, algae and several bacteria. In the proposed research the electron transfer dynamics will be accessed directly by the unique CD signature of the RC as it contains several strongly coupled pigments.

FY 2014 HIGHLIGHTS

Four papers and a book chapter were published based on the results of this research in FY 2013. Main achievements:

- 1) Triplet state energies and lifetimes of almost all natural (bacterio)chlorophylls have been characterized by means of ultrasensitive home-built time-gated phosphorescence spectrometer and supplemented by respective quantum mechanical calculations (J. Phys. Chem. B 2014, 118:7221-7232).
- 2) Oxygen concentration within a functioning photosynthetic cell was estimated by means of diffusion theory based on experiment data. This has both evolutionary importance as well as experimental importance for future research (Biophysical J. 2014, 106, p.1882-1889).
- 3) The heterogeneity of dielectric constant in an electron transfer protein cytochrome b6f has been demonstrated and its functional importance outlined (J. Phys. Chem. B, 2014, 118: 6614-6625).

- 4) The photosystem II reaction center complex was analyzed and it was shown that most of the groups in the past worked on a damaged system that questions the validity of several conclusions on electron transfer in this important complex (Phys. Chem. B 2014)
- 5) A review chapter on charge separation complexes was published in a book (Savikhin S, Jankowiak R, 'Mechanism of Primary Charge Separation in Photosynthetic Reaction Centers', in: 'The Biophysics of Photosynthesis', Eds. John Golbeck & van der Est, 2014)/
- 6) A work started on building the TRCD spectrometer: the pump laser and other necessary equipment was ordered for the 2014-2015 project

Improved Efficiency of Energy Capture and Conversion by Regulating the Interaction Between ATP Synthesis and End Product Synthesis

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 Funding: \$170,000 (2014)

PROGRAM SCOPE

The last step of photosynthetic carbon fixation, the first production of starch and sucrose (“end products”), can regulate the overall rate of photosynthesis. This project makes use of genetically engineered plants and variations in measurement conditions (temperature, carbon dioxide etc.) to explore the regulation of photosynthesis that results in efficient energy capture and conversion. The goal is to learn how this regulation works and to determine opportunities for improving the regulation to better adapt plants to bioenergy production. In addition, the physical separation of the two main end product pathways (starch and sucrose synthesis) can be eliminated by expressing a glucose 6-phosphate (G6P) transporter (GPT2) with an unregulated promoter.

FY 2014 HIGHLIGHTS

The GPT2 antiporter was overexpressed in *Arabidopsis* by placing the cDNA of GPT2 behind a 35S promoter. Four transgenic lines as well as an empty vector control were generated and the line with the highest expression level was carried forward for physiological experiments. When daytime light levels were constant, growth of the GPT2 overexpressing line was similar to WT or empty vector controls, although the flowering is a week to two weeks delayed. However, when the amount of light given to the plant is increased by as little as $20 \mu\text{mol m}^{-2} \text{s}^{-1}$, the transgenic plants show a large reduction in growth. The GPT2 overexpressing lines accumulate large amounts of anthocyanins within five days of the change in light level and an immediate increase in starch synthesis and degradation. The increase in starch persists in these plants so that by flowering they have four to five times the amount of starch in the leaves as the empty vector controls. The high starch amounts in the GPT2 overexpressing lines have led us to hypothesize that G6P is being imported into the chloroplast during the day. The increased G6P concentration in the chloroplast as a result of import by GPT2 could be high enough to overcome the high K_m of G6PDH for G6P. This would cause a G6P shunt around the Calvin-Benson cycle and require additional input of ATP. We found that cyclic electron transport was higher in GPT2 overexpressing plants and was increased even further in plants transferred from growth at $70 \mu\text{mol photons m}^{-2} \text{s}^{-1}$ to $190 \mu\text{mol photons m}^{-2} \text{s}^{-1}$ at five weeks and measured three weeks after the shift. This finding caused us

to change priorities to pursue the importance of the G6P shunt around the Calvin-Benson cycle. We were able to get preliminary evidence that it may explain a number of anomalous observations reported in the past and that the G6P shunt plays an important role in stabilizing photosynthesis, especially in fluctuating light.

Structure/Function of the Novel Proteins LCIB and LCIC in the *Chlamydomonas* CCM

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PROGRAM SCOPE

LCIB, a novel protein of unknown function, is an essential component of the CO₂-concentrating mechanism (CCM) required by microalgae to grow in environments where available CO₂ is at or below air equilibration levels. Microalgae, together with cyanobacteria, are responsible for approximately half of the earth's primary photosynthetic productivity, and because of their photosynthetic CO₂ assimilation efficiency and high productivity, microalgae are a viable, solar energy driven source for conversion of CO₂ to renewable biofuel and other renewable bioproducts. We have only a limited understanding of the biological function underlying these applications, especially regarding our understanding of the functional components and detailed mechanisms comprising the microalgal CCM – an essential system for photoautotrophic growth. Identification in *Chlamydomonas reinhardtii* (*Chlamydomonas*) of essential CCM components, including LCIB, has improved our knowledge of the microalgal CCM, but significant gaps in our understanding still exist. Because LCIB is a novel, soluble chloroplast stromal protein lacking any recognizable domains or any apparent homologs outside of the “green lineage” algae (e.g., green algae and diatoms), and a small number of cyanobacteria and bacteria, the specific nature of its critical role in the CCM still is somewhat unclear. However, the observation that LCIB homologs are found in all algae with both sequenced genomes and demonstrated CCMs, argues for an important role in algal CCMs in general, as well as in enhancing microalgal CCMs to enable sustainable, efficient microalgal production of biofuels and other renewable bioproducts. Our hypothesis is that a key CCM complex, formed from LCIB and the similar protein LCIC, participates in an active CO₂ accumulation pathway that acts through vectorial hydration of CO₂ to bicarbonate to capture and concentrate external CO₂ diffusing into the cell for enhanced CO₂ assimilation in low CO₂ conditions.

FY 2014 HIGHLIGHTS

We identified two mutants of LCIC, which forms a functional complex with LCIB. They reveal that LCIB can form a functional complex in the absence of LCIC but that LCIC is required for relocalization of the LCIB/LCIC complex under very low CO₂ conditions. LCIC mutants show moderate decreases in CO₂-dependent photosynthetic O₂ evolution but grow fairly well in low CO₂ and very-low CO₂. It appears that LCIC is not essential for CCM function but may enhance CO₂ assimilation in very low CO₂ conditions. LCIB mutants have an “air-dier” phenotype; they are able to grow in either 5% CO₂ or very-low-CO₂, but cannot survive air-level CO₂. We identified a mutant defective in LCIA, a putative bicarbonate transporter, which is unable to survive in very low CO₂ when combined with an LCIB mutation. This

suggests that both LCIA and LCIB are needed for very low CO₂ survival, although neither individual mutation caused very low CO₂ growth defects. Both are essential for very low CO₂ acclimation, but LCIB and LCIA appear to function in active CO₂ uptake and bicarbonate transport, respectively. Based on these contrasting and complementary roles of LCIA and LCIB, we proposed a mechanism to explain differential regulation of the CCM based on CO₂ inhibition of bicarbonate transporters in air-level CO₂ conditions. We also used novel gene activation technology (TALEs), to selectively activate expression of the putative bicarbonate transporter, HLA3. In high-CO₂, where it is normally repressed, HLA3 overexpression modestly increased photosynthetic CO₂ assimilation only at very low CO₂ concentrations, and combined overexpression of HLA3 and LCIA caused a more significant increase in photosynthetic CO₂ assimilation, suggesting synergistic function of HLA3 and LCIA. These results are consistent with our hypothesis that bicarbonate transporters play a significant role in the CCM only when CO₂ concentrations are too low to support LCIB-facilitated CCM activity.

Role of the Rubisco Small Subunit

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

Ribulose-1,5-bisphosphate carboxylase/oxygenase (Rubisco) catalyzes the rate-limiting step of photosynthesis, but it is one of the slowest enzymes. O₂ also competes with CO₂ at the enzyme's active site, and oxygenation initiates the photorespiratory pathway that leads to the release of CO₂. If carboxylation could be increased or oxygenation decreased, an increase in net CO₂ fixation would be realized. There is much interest in engineering Rubisco to increase the production of food and renewable energy. However, it is difficult to engineer plant Rubisco because the polyploid chloroplast genome encodes the active-site large subunits, and a family of nuclear genes encodes the small subunits. All of these gene copies can be eliminated in the green alga *Chlamydomonas reinhardtii*, which is the only eukaryotic model system that allows genetic engineering of both subunits. The goal of this project is to understand the structure-function relationships of the eukaryotic small subunit as a means for ultimately improving Rubisco. Analysis of the variable betaA-betaB loop by genetic selection, directed mutagenesis, and construction of chimeras, has shown that the small subunit can influence CO₂/O₂ specificity and catalytic efficiency even though the active site resides in the large subunit. X-ray crystal structures of engineered chimeric-loop enzymes indicated that additional residues and regions of the small subunit may also contribute to Rubisco function. To identify such regions, the most-conserved small-subunit residues were analyzed by alanine-scanning mutagenesis. From that work, a structural pathway was discovered between the betaA-betaB loop and alpha-helix 8 of the large-subunit active site. Hybrid enzymes have also been created comprised of plant small subunits and *Chlamydomonas* large subunits, and these enzymes have increases in CO₂/O₂ specificity, further indicating that small subunits may be the key for ultimately engineering an improved Rubisco enzyme.

FY 2014 HIGHLIGHTS

The betaA-betaB loops from each of four small subunits at the top and bottom of the holoenzyme define the opening of a solvent channel that passes through the large-subunit core. To determine whether the central solvent channel may play a role in holoenzyme function, substitutions were made at Ile-58, which defines the narrowest diameter of the channel opening. Single substitutions had little or no effect, but, when three Trp residues were introduced in place of Ile-58 (introducing 12 Trp residues from four small subunits), CO₂/O₂ specificity and holoenzyme thermal stability were decreased. These results indicated that the small-subunit betaA-betaB loop might influence large-subunit catalysis by altering the conformational change in the holoenzyme that occurs during catalysis. However, because the mutant enzyme was found to be activated normally, it might instead be possible that the channel plays a role in diffusion of CO₂ and O₂ to the Rubisco active site. In a second area of study, Ala-scanning mutagenesis of the most conserved small-subunit residues identified Y32A as the only mutant substitution outside of the betaA-betaB loop that affects CO₂/O₂ specificity. Tyr-32 shields the carboxyl-terminal end of large-subunit alpha-helix 8 from solvent. Y32A, Y32D and Y32E substitutions decrease CO₂/O₂ specificity and holoenzyme thermal stability *in vivo* and *in vitro*, but Y32F and Y32R substitutions do not. It seems likely that either a phenolic ring or positive charge complements the partial negative charge at the carboxyl-terminal end of alpha-helix 8. This interaction may influence the position or amino-terminal charge of alpha-helix 8, which, in turn, may influence interactions between amino-terminal alpha-helix-8 residues and the carboxylation transition state. These results can explain how changes far from the active site affect catalytic efficiency.

RNA Quality Control in the Chloroplast

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Funding: \$165,000 (2014)

PROGRAM SCOPE

RNA molecules serve either as templates for protein production, or function directly in the form of RNA. These so-called non-coding RNAs may influence gene expression by binding to chromosomes, activating RNA interference pathways, binding metabolites to regulate related operons, or pairing with messenger RNAs to activate or repress their translation into proteins. Our project focuses on the chloroplast, where photosynthesis occurs, and how these various RNA populations are created and managed. Functional RNAs must have the correct length and sequence composition. For example, intron-containing RNAs cannot be translated, and long antisense RNAs can have undesirable impacts on gene expression. RNA quality control is a term that describes the mechanisms by which organisms differentiate between functional and unwanted RNAs, and dispose selectively of the latter. Our approach is to analyze chloroplast RNA populations, and the enzymes that act on them, in different fractions of the chloroplast. Our hypothesis is that the spatial separation of ribonucleases within the chloroplast underpins quality control. Thus, quality control is proposed to be exerted as an RNA progresses along a pipeline from the site of transcription to the site of gene expression. To test this, we are using high-throughput RNA sequencing (RNA-seq) which identifies quantitatively and separately sense and antisense RNAs. We are also using mutants defective in particular RNases to verify their roles in quality control.

FY 2014 HIGHLIGHTS

Our major accomplishments fall into two categories: bioinformatics and RNA analysis. In the area of bioinformatics, we have developed a customized and user-friendly pipeline to analyze next-generation sequence data for chloroplast expression. The pipeline extracts chloroplast reads, aligns them to the chloroplast genome, and allows quantitative analysis of transcript abundance. Furthermore, efficiency of intron removal (splicing) and RNA editing can be routinely evaluated. Parallel use of the pipeline on multiple datasets allows comparative RNA analysis. We have used this capability to 1) compare RNA populations in different subfractions of the chloroplast; 2) compare RNA populations in plants deficient in specific chloroplast ribonucleases with their wild-type counterparts; and 3) extract data from published datasets where chloroplast reads had been disregarded. Our most complete analysis in 2014 was of a mutant lacking a double-strand-specific ribonuclease called mini-III. No organellar ribonuclease of this type had previously been described. We discovered that chloroplast Mini-III has multiple roles including ribosomal RNA maturation, intron recycling and regulation of at least one antisense RNA. Thus, to summarize, our accomplishments are highlighted by development of a generally useable chloroplast NGS pipeline, and its application to study the metabolism of double-stranded RNA in the chloroplast.

Structure-Function Relationships of Regulator Proteins That Control Photosynthetic Carbon Dioxide Fixation in Nonsulfur Purple Bacteria

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Funding: \$70,000 (2014)

PROGRAM SCOPE

The overall objective of this project is to determine the mechanism by which a transcriptional activator protein affects CO₂ fixation (*cbb*) gene expression in nonsulfur purple photosynthetic bacteria, with special emphasis to *Rhodobacter sphaeroides* and with comparison to *Rhodospseudomonas palustris*. In *Rb. sphaeroides*, CbbR and RegA (PrrA) are transcriptional regulators of the *cbb_I* and *cbb_{II}* (Calvin-Benson-Bassham) CO₂ fixation pathway operons. We find that both proteins interact specifically with promoter sequences of the *cbb* operons, a rather unique situation for unrelated regulator proteins. RegA has four DNA binding sites within the *cbb_I* promoter region, with the CbbR binding site and RegA binding site 1 overlapping each other. Previous results showed that these transcriptional regulators interacted to form a specific RegA-CbbR complex on the DNA and we established that CbbR must first bind to the DNA at its specific binding site before RegA could interact with the CbbR-DNA complex. Over the past year, we have completed studies to define the residues in RegA that are required for specific interactions with CbbR, which is bound to the DNA. Exhaustive mutational analysis has established that RegA and CbbR interact through their DNA binding domains (DBDs). Most DBDs are connected to their “effector” domains through rigid linker helices or small linkers that prevent interactions between domains. Commonly, DBDs are either at the N-terminus or C-terminus of the protein, as is the case with CbbR and RegA, located at the N-terminus and at the C-terminus, respectively. Mutational analysis of the DBD of RegA has identified many single amino acid mutations located in the helix-turn-helix region of RegA (α -helix 7, α -helix 8 and the small turn region between the two helices) that abolish or severely

reduce the interaction with CbbR. As with the mutations in the receiver domain, a loss of interaction with CbbR is accompanied with a reduction in DNA binding.

FY 2014 HIGHLIGHTS

1. Farmer, R. M., Laguna, R., Panescu, J., McCoy, A., Logsdon, M., Zianni, M., Moskvina, O. V., Gomelsky, M., and Tabita, F. R. Altered residues in key proteins influence the expression and activity of the nitrogenase complex in an adaptive CO₂ fixation deficient mutant strain of *Rhodobacter sphaeroides*. *Microbiology* 160 (2014) 198-208.
2. Dangel, A. W., Luther, A., and Tabita, F. R. Amino Acid Residues of RegA Important for Interactions with the CbbR-DNA Complex of *Rhodobacter sphaeroides*: DNA Binding Domain Interactions. *J. Bacteriol.* 196 (2014) 3179-3190.

Energetics and Mechanisms of Protein Transport and Energy Transduction in Chloroplasts

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Funding: \$170,001 (2014)

PROGRAM SCOPE

The long-term goal of the research in my laboratory has been to understand the mechanisms through which protein targeting is accomplished in both prokaryotic and eukaryotic cells. We have often made use of bioenergetics as a window into these processes. This necessarily includes consideration of the manner in which energy is initially transduced and converted into biologically useful forms (i.e., proton motive force and ATP). The experiments of this proposal are aimed at quantitating the energy required by chloroplast protein targeting reactions and discovering the principles through which the energy input is controlled. To this end we proposed quantitating the amount of energy utilized by two pathways the transport proteins into or across the thylakoid membranes. Our experiments also address the question of the use of localized protons for photophosphorylation and for protein transport across the thylakoid membrane.

FY 2014 HIGHLIGHTS

For the fiscal year 2014 we made the most progress on the second of the two goals for the proposal. After many unsuccessful attempts to generate stable plants in which a pH-indicating GFP protein resides in the thylakoid lumen, we moved to examining the signal from this protein delivered by *in vitro* protein targeting techniques. After import of pH indicating GFP into the thylakoid lumen, these thylakoids were subsequently used to monitor light-induced pH changes taking place in the lumen space. We found the signal from the GFP responded to the lower pH caused by light in predictable ways, and recovered its original qualities after cessation of illumination. We continue to develop this technique as a reliable indicator of light-induced pH changes in the lumen. We also completed a project in which we asked whether thylakoids can divide independently of the chloroplast division machinery. By examining thylakoid structure in well-characterized chloroplast division mutants, we have shown the thylakoids do not appear to possess their own independent division machinery.

EARLY CAREER: Residue Specific Characterization of Electrostatics, Conformational Heterogeneity, and Dynamics of Electron Transfer Proteins with Linear and Nonlinear Infrared Spectroscopy

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PROGRAM SCOPE

Electron transfer reactions are central to life as they underlie the harvesting, storage, and retrieval of the energy required to sustain it. Unlike electron transfer between small molecules, biological electron transfer occurs between redox centers imbedded within proteins with environments that are structurally and electrostatically heterogeneous and undergo fluctuations on a broad range of timescales. Furthermore, inter-protein electron transfer requires protein-protein binding that is transient to maintain rapid turnover, but sufficiently specific to precisely control electron flow. Unfortunately, the rigorous characterization of biological electron transfer has proven challenging with currently available techniques as they are incapable of resolving dynamics on a sufficiently fast timescale, and/or because they are incapable of specifically probing different parts of the electron transfer complexes. This project overcomes both of these challenges by 1) employing recent advances in the techniques of linear and nonlinear infrared spectroscopy that are uniquely capable of quantifying conformational heterogeneity and fast motion in proteins, and 2) employing recent advances in protein production that allow for the incorporation of nonperturbative local probes that will enable the spectroscopic studies to report on specific parts of a protein or protein complex. This approach is applied toward delineating the nature of the physiologically central complex between plastocyanin (Pc) and cytochrome f (cyt f), two key electron transport proteins of the photosynthetic apparatus. These studies will aim to develop a picture of the electrostatics, conformational heterogeneity, and dynamics of electron transfer proteins, and how they conspire to mediate the efficient and specific electron transfer.

FY 2014 HIGHLIGHTS

The Cu redox center of Pc has been characterized through the incorporation of carbon deuterium (C-D) bonds as site-specific, frequency-resolved probes of the protein. This past year, (methyl-d₃)-methionine was incorporated as an axial ligand to the Cu center using mutagenesis and expression in labeled media. FTIR spectroscopy of the stretching frequency of the C-D bond has shown that the probe is sensitive to cyt f binding, the redox state of the Cu, substitution of Cu for Zn, and displacement of histidine Cu ligands by changing pH, despite that the Met-Cu bond is considered very weak for type I Cu centers like found in Pc. For example, significant shifts to lower frequency were observed upon reduction of Pc, which is consistent with increased σ donation of the S centered orbitals of Met to the Cu, resulting in increased electron withdraw from the C-D bond. The C-D frequency showed greater dependence on changes to the redox center in comparison to cyt f binding, but suggested that upon binding cyt f the redox environment becomes more polar and less heterogeneous. In addition, the amber codon suppression method was used to incorporate p-cyanophenylalanine (CNPhe) as a probe of the binding surface of Pc with cyt f. Three residues located along the binding interface of Pc have been successfully

substituted with CNPhe. FTIR characterization of CNPhe labeled at Tyr89, which located in the “electrostatic patch” of Pc, displayed a reduction in linewidth upon binding to cyt f, suggesting a decrease in conformational heterogeneity. In addition, the incorporation of (phenyl-3,5-d₂)-tyrosine is being employed to provide completely non-perturbative characterization of the proteins and gauge the potential perturbation induced by the CN probes. Finally, 2D-IR experiments of the CNPhe-labeled Pc have been initiated to characterize the site-specific dynamics and how they might be impacted by the redox state and/or interaction with cyt f.

Thylakoid Membrane Biogenesis in Cyanobacteria

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

We have observed that upon extended dark-incubation followed by illumination of a cyanobacterial mutant that is unable to synthesize chlorophyll in darkness, thylakoids are synthesized rapidly upon illumination. Indeed, we have been able to capture images of biosynthesis intermediates in the process that suggest that thylakoid membranes can originate from large membrane-enclosed vesicles in the cells. Moreover, we have developed and refined an *in vivo*, stable-isotope labeling method to determine whether proteins and lipids are newly synthesized or are utilized from existing pools. We now are in an excellent position to stepwise follow thylakoid membrane biogenesis and to elucidate the nature of vesicles and protein components involved. The theme of the research is thylakoid biogenesis, with as secondary theme the integration of proteins into thylakoids. The research includes (1) identification of proteins and processes involved in thylakoid membrane formation upon illumination of the *chlL*- strain that is impaired in chlorophyll biosynthesis in darkness; and (2) determination of the role of the VIPP-1 protein and chaperones that it potentially interacts with (DnaK, DnaJ and Slr1641 (ClpB1)) in thylakoid membrane biosynthesis. The research utilizes a variety of experimental approaches, including overexpression of key proteins in *Synechocystis* and its mutant strains, determination of *de novo* biosynthesis by means of *in vivo* isotope labeling, and ultrastructural (electron microscopy) studies to follow membrane biogenesis processes.

FY 2014 HIGHLIGHTS

We followed the process of chlorophyll, lipid and protein biosynthesis and recovery of thylakoids and photosynthetic function in a strain of *Synechocystis* that cannot make chlorophyll in darkness and that had been grown in virtual darkness for two weeks before being exposed to continuous light. Shortly before exposure to light, ¹³C-glucose was added to the culture, and the amount of labeled (newly synthesized) vs. unlabeled (pre-existing) chlorophyll, proteins, and lipids was determined by removing samples from the culture at regular intervals after the start of illumination, and isolating the various components. Proteins were size-fractionated on a gel, and pieces of the gel were washed and treated with trypsin. Recovered protein fragments were separated by LC-MS, and the origin of prevalent fragments was identified. About 160 different soluble and membrane proteins have been identified in our labeling experiments. PS I core proteins initially are virtually absent because of the lack of

chlorophyll, and are then synthesized rapidly. In contrast, most PS II proteins are found in darkness but are rapidly degraded in the light and then new synthesis starts. However, lipids as well as many proteins unrelated to photosynthesis remained rather unlabeled for the first 4 hours and then were labeled to the degree expected from the growth of the culture, indicating that lipids already pre-existed in dark-grown cells even though there were not many membranes yet. Our hypothesis is that large lipophilic bodies found in dark-grown cells contain lipids that are used for thylakoid membrane biosynthesis.

Structure and Assembly of Rubisco Activase

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Funding: \$195,000 (2014)

PROGRAM SCOPE

This project addresses the regulation of carbon fixation by Rubisco activase (Rca), a chemo-mechanical motor protein essential in maintaining Rubisco activity. The goal of this work is to elucidate three-dimensional structures of higher plant Rcas and to investigate their interaction with Rubisco. Long-term, we are interested in gaining a full understanding of the mechanism of Rubisco remodeling. The extremely abundant enzyme Rubisco catalyzes the incorporation of CO₂ into simple carbohydrates, thus generating the necessary precursors for hexose biosynthesis. *In vitro*, higher plant Rubisco activity decreases with time, in large part due to the turnover-dependent production of substrate mimics that function as tight-binding competitive inhibitors. In addition, decarbamylation of a catalytic lysine residue leads to the formation of inhibitory complexes with the substrate ribulose-1,5-bisphosphate. In many photosynthetic organisms, the ATPase activity of Rca stabilizes the open form of Rubisco, so that Rubisco sites become available for CO₂ fixation. Rca belongs to a group of P-loop ATPases that tend to operate in ring-like assemblies to conformationally remodel their partner proteins. Rca activity is thought to be regulated by the ambient ATP/ADP ratio in the chloroplast stroma, and in longer isoforms, by the stromal redox poise. Therefore, Rca embodies an important biological check point responsible for maintaining Rubisco turnover under stromal conditions of high energy charge, and for keeping Rubisco inactivated under less favorable conditions.

FY 2014 HIGHLIGHTS

Accomplishments for 2014:

Rubisco subunit assembly: ATP and magnesium promote cotton Rca hexamer formation at low micromolar concentrations. We have C-terminally labeled cotton Rca with an Alexa-Fluor dye, and have developed fluorescence correlation spectroscopic (FCS) methods to determine individual binding constants for the step-wise assembly of Rca subunits. We have applied these methods to study Rca assembly as a function of adenine nucleotide composition. Results obtained for wild-type cotton Rca were confirmed by comparison to the catalytically impaired substrate-trap mutant Walker B-D173N in the presence of Mg•ATP. Our data support the stabilization of biologically relevant closed-ring hexameric forms by ATP, whereas ADP facilitates a more continuous assembly pathway such as spirals. A titration with free magnesium ions provides evidence that hexameric forms are favored at high magnesium at the expense of supramolecular aggregates. These results suggest that a second

magnesium ion binding site with an equilibrium constant of 1-3 mM promotes subunit contacts critical for formation of toroidal assemblies.

Mechanistic enzymology of tobacco Rca: ADP inhibition, cooperativity and activation. To examine the regulation of Rca activity by the available ATP and ADP pool, we have developed a continuous enzyme-coupled ATPase assay that monitors phosphate production and tolerates moderate amounts of ADP in the reaction mixture. We have measured initial velocities as a function of ATP concentration for a variety of Rca preparations, and have fit the data to a steady state turnover kinetic model. In this way, we have determined turnover numbers, Michaelis constants, Hill coefficients, product inhibition constants and magnesium binding constants.

DOE National Laboratories

Functional Models of Photosynthetic Light Harvesting Systems Templated by Self-Assembling Proteins

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Funding: \$582,000 (2014)

PROGRAM SCOPE

Photosynthetic organisms rely on a series of complex light harvesting systems to absorb broad spectrum light and transfer the resulting excitations to the reaction centers. Determining the key features that enable the unparalleled energy transduction efficiencies of these systems is paramount to our ability to harness and mimic them in the context of photocatalytic materials and optical sensors. The full and detailed theoretical understanding of photosynthetic light harvesting has remained elusive, however, due to our inability to determine the individual contributions of the many functional components that must work in concert to yield higher-level function. Additionally, the effects of protein dynamics and conformational disorder on the performance of these systems are poorly understood and often overlooked. This program is thoroughly examining these aspects by combining extended electronic structure calculations with dynamical simulations that span multiple time and length scales. The predictions of these models are then being validated spectroscopically using a well-defined experimental model in which chromophore arrays can be generated with readily specified distances, orientations, and interactions with the protein environment. The models and approaches developed through this program will inform the design of new artificial systems and also suggest the features responsible for the high quantum efficiencies exhibited in natural photosynthesis. This program will also yield a highly adaptable set of synthetic scaffolds that are accompanied by an unprecedented level of theoretical understanding. This combination will allow the design of future materials that integrate multiple types of interacting components into well-defined three-dimensional frameworks.

FY 2014 HIGHLIGHTS

1. Francis has generated two protein platforms for displaying multiple chromophores with defined distance relationships. They have also developed new methods to specify the numbers of

pigments. These efforts have provided some of the first available measurements of homogeneous and systematically varied chromophore arrays, allowing protein-pigment and pigment-pigment interactions to be evaluated on a separate basis.

2. Ginsberg has performed transient absorption studies of the Francis protein assemblies, which were sparsely labeled with dye molecules on their hydrated interiors. These studies showed that the environments of the chromophores can be tailored to reduce non-radiative decay pathways substantially.
3. The effects of rigidified linking groups have been elucidated by Francis using a new synthetic strategy for chromophore attachment. These studies have validated that the chromophore geometries can be altered to improve energy transfer performance.
4. Neaton has studied the electronic structures of unique chromophore monomers and dimers designed and synthesized by the Francis lab using TDDFT. They have shown that the ideal dipole and Heitler London approximations are not sufficient to describe the coupling between neighboring chromophores.
5. Neaton has explored the state manifold near strongly absorbing excited states on chromophores for which transient absorption spectra have been collected by the Ginsberg lab. They have shown that there are significant dipole changes between ground and excited states, implying that reorganization energies, and therefore environmental influences upon de-excitation pathways, may be significant.
6. Using molecular simulations of the double-layer protein disks prepared by Francis, Geissler has examined how the dynamical environment of a bound chromophore varies with its attachment site. Extensive comparisons were made with Ginsberg's measurements of these experimental systems.

Photobiological and Photobiohybrid Solar Fuels: Photobiological Component

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Funding: \$437,000 (2014)

PROGRAM SCOPE

Photosynthetic systems are regulated by a number of mechanisms that act at different points during the process of light transduction into chemical energy. The goal of this project is to investigate the regulation of photosynthetic reductant partitioning between H₂ evolution, biomass accumulation, and the production of other storage molecules. We are interested in the mechanism of interaction between different signal/sensors, sensors/transducers, and the complex networks between those and the expression of specific genes of interest. This project consists of two subtasks addressing, respectively, (a) regulation of photosynthetic reductant partitioning between CO₂ fixation and hydrogenases under anaerobic conditions; and (b) regulation of reductant and carbon partitioning between biomass and carbon storage molecules under N and other stresses.

FY 2014 HIGHLIGHTS

We previously showed that a cyanobacterial mutant that is unable to store carbon as glycogen upon nitrogen deprivation secretes pyruvate and alpha-ketoglutarate (AKG), instead. Production of pyruvate releases additional ATP, while production of AKG releases additional NADH. When grown under different light intensities and then transferred to nutrient-depleted medium, the ratio of secreted pyruvate/AKG varied as a function of light intensity: high light, which activates cyclic electron flow and produces more ATP, resulted in lower pyruvate/AKG; conversely, under low light, the cells secreted a higher ratio of pyruvate/AKG. These results suggest that carbon partitioning is regulated by upstream photosynthetic activity, and that this regulation is possibly mediated by a pathway that senses the ATP/NAD(P)H intracellular ratio. Efforts are under way to actually determine the rates of cyclic and linear electron transfer in the mutant, and to measure ATP and NADPH *in vivo*, in collaboration with Graham Peers, Colorado State University and Rob Burnap, Oklahoma State University.

Carrieri, D., Broadbent, C., Carruth, D., Paddock, T., Ungerer, J., Maness, P.C., Ghirardi, M. and Yu, J. "Enhancing photo-catalytic production of organic acids in the cyanobacterium *Synechocystis* sp. PCC 6803 DglgC, a strain incapable of glycogen storage. 2014. *Microb. Biotechnol*, DOI: 10.1111/1751-7915.12243.

Photobiological and Photobiohybrid Solar Fuels: Photobiohybrid Project

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Funding: \$873,000 (2014)

PROGRAM SCOPE

Photosynthetic light-capture and conversion efficiencies in plant-type systems are constrained at ~12.5% photon-to-fuel due to narrow spectral bandwidth, low-light saturation kinetics and thermodynamic losses during energy transduction. Complex regulatory mechanisms provide additional elements of control via coupling between photosynthetic electron transport and downstream metabolic reactions. Simplifying the complexity of photosynthetic systems is one strategy toward improving conversion efficiencies. We have been investigating how semiconducting nanomaterials that exhibit wide spectral responses and high saturation intensities can be utilized to create molecular systems for artificial photosynthesis and production of reduced fuels. To create and control the essential charge-transfer interactions between synthetic chromophores and biocatalysts requires developing a broader understanding of energy transduction processes at molecular junctions. This project integrates fundamental research on structure-function mechanisms of enzymatic H₂ activation, with steady-state and ultrafast measurements of photochemical conversion in enzyme-nanoparticle biohybrids. The knowledge will help elucidate the physical, thermodynamic and kinetic parameters that control efficiencies of light-harvesting, charge-transfer and catalysis in molecular systems for solar hydrogen production.

FY 2014 HIGHLIGHTS

The *Chlamydomonas reinhardtii* [FeFe]-hydrogenase (CrHydA1) is a naturally minimized structure with only a catalytic H-cluster and is an ideal model to investigate mechanisms of H₂ activation by this class of hydrogenases. During this period we analyzed a proton-transfer mutant of CrHydA1 by EPR and FTIR spectroscopy under catalytic conditions. The H₂ binding and activation by the H-cluster involved a diferrous 2Fe subcluster and [4Fe-4S]¹⁺ subcluster, and formation of a terminal hydride (H) species with H/D isotope-sensitive IR signals. The results also show that H-cluster redox transitions are strongly coupled to proton-transfer. Mulder, D.W.; Ratzloff, M.W.; Bruschi, M.; Greco, C.; Koonce, E.; Peters, J.W.; and, King, P.W. 2014. J. Am. Chem. Soc. DOI: 10.1021/ja508629m.

The free energies along proton-transfer (PT) pathways in [FeFe]-hydrogenase were investigated using QM/MM and umbrella sampling techniques. Key residues including a conserved H-cluster proximal Cys were identified, and the pK_a values were estimated from a thermodynamics integration method, which together were used to model the PT profiles to the H-cluster. H. Long, P.W. King, C.H. Chang. 2014. J. Phys. Chem. B. 118:890.

The [FeFe]-hydrogenase from *Clostridium acetobutylicum* (CaI) self-assembles with semi-conducting nanoparticles (NP) to form photocatalytic complexes. NP light adsorption and charge-separation leads to interfacial electron-injection into the bound CaI at a surface localized [4Fe-4S]-cluster at rates of ~10⁷ s⁻¹. Changes in NP diameter control the internal charge recombination kinetics and the free-energy of interfacial electron-transfer, and we investigated how diameter affects k_{ET} and H₂ production. Surprisingly, the electron-transfer step was minimally affected by changes in free-energy. As a result, H₂ production rates were largely controlled by competition with NP internal recombination, which are slower in larger NPs to allow for higher quantum yields of H₂.

An Integrated, Super-Resolution Characterization of Natural Photosynthesis. Operating Principles, Structure, Regulation and Repair

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Funding: \$902,000 (2014)

PROGRAM SCOPE

In plants and algae, a dynamic network of photosynthetic membranes forms inside chloroplasts, responds to changing light levels and spectral composition, regulates the balance of activities of the two photosystems, and repairs and replaces critical components as they are damaged by photo-oxidation. By integrating programs in plant genetics, biophysics, advanced imaging, ultrafast spectroscopy, engineering, and computational modeling, our goal is to obtain a detailed molecular description of the organization of the thylakoid membrane, the regulation of its composition, and the membrane dynamics occurring during its biogenesis, regulation and repair. We follow protein rearrangements in

photosynthetic membranes using a range of cutting-edge imaging techniques, which are ideally suited to reveal the complex structural dynamics of the membrane at different levels of spatio-temporal resolution. The imaging approaches are integrated with parallel modeling and theoretical efforts, which will provide new insights into the fundamental biophysical mechanisms governing protein interactions and the partitioning of protein complexes in the photosynthetic membrane.

FY 2014 HIGHLIGHTS

Atomic force microscopy (AFM) was used to visualize photosystem II (PSII) supercomplexes in grana membranes from *Arabidopsis*. We developed a statistical image analysis pipeline to discriminate disordered from crystalline particles in an unbiased fashion and classify crystalline arrays according to their unit cell properties. We found evidence that interactions among light-harvesting antenna complexes are altered in the *soq1* mutant, which affects regulation of light harvesting. Using a customized AFM with integrated fluorescence imaging, we directly characterized the dynamic changes in biophysical properties of the thylakoid membrane during a state transition. The elasticity (stiffness) of the thylakoid membranes increased immediately upon PSII-specific illumination, followed by a delayed height change. Electron microscopy was used to corroborate changes in membrane-to-membrane spacing. While the change in stiffness depended primarily on the transmembrane pH gradient, the height change required both a pH gradient and STN7-dependent phosphorylation. We are developing a novel near-field optical scanning microscopy that uses a cathodoluminescent film to combine the high spatial and temporal resolution of a scanning electron microscope with the non-invasiveness of light microscopy at length scales well below the diffraction limit. Fluorescence microscopy was used to identify *Chlamydomonas* mutants with altered formation or organization of the thylakoid network. Using a coarse-grained model of transmembrane alpha helices, we showed that hydrophobic mismatch between the membrane and the protein is the dominant factor determining transmembrane helix packing and the crossing-angle distribution of transmembrane helices.

Regulation of Photosynthesis

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Funding: \$582,000 (2014)

PROGRAM SCOPE

Photosynthetic light-harvesting systems are regulated, protected against photo-oxidative damage, self-assembled into supercomplexes, and rely on a subtle balance of electronic interactions to produce a highly robust system. In this project, we apply a multidisciplinary approach that combines genetic and biochemical techniques with ultrafast spectroscopy to understand the mechanisms by which oxygenic photosynthetic organisms regulate the efficiency of light harvesting in Photosystem II. In response to fluctuations in light intensity, nonphotochemical quenching (NPQ) mechanisms that regulate photosynthetic light harvesting are induced. In algae and plants, the qE type of NPQ is turned on and off rapidly by changes in thylakoid lumen pH, whereas the slower qI type downregulates PSII during long-term light stress. Our specific aims are (1) to investigate a novel type of violaxanthin de-epoxidase (VDE) enzyme in *Chlamydomonas*, (2) to identify the structural features that make LHCSR a qE-quenching

protein instead of a light-harvesting protein, (3) to assess the roles of LHCSR (and PsbS) in other algae, (4) to gain new insight into q1 in *Arabidopsis*, and (5) to develop predictive computational models of excitation energy transfer and NPQ.

FY 2014 HIGHLIGHTS

By complementing the *Arabidopsis npq1* mutation with the NPQ1 gene of *Chlamydomonas*, we showed that the NPQ1 protein is indeed a functional VDE. Furthermore, we were able to complement both the *Chlamydomonas* and *Arabidopsis npq1* mutations with a carboxyl-terminal epitope-tagged NPQ1 protein, and cellular fractionation experiments showed that, unlike the plant-type VDE, NPQ1 is a stromal protein associated with thylakoid membranes. By site-directed mutagenesis, we identified three lumen-facing, acidic residues in LHCSR3 that are necessary for its function in qE. Mutagenesis techniques were established for the green alga *Chromochloris zofingiensis*, which has an unusually high NPQ capacity, and for the heterokont alga *Nannochloropsis oceanica*, and npq mutants of both species were isolated. We identified suppressors of the soq1 mutation in *Arabidopsis*, which encodes a thioredoxin-like protein that is involved in a novel type of antenna q1. Using an apparatus for measuring fluorescence lifetime snapshots during induction of qE, we showed that PsbS changes the amount of quenching and the rate at which quenching turns on, but it does not affect the relaxation dynamics of excited chlorophyll during quenching. In contrast, the presence of VDE, which is necessary for the accumulation of zeaxanthin, affects the excited-state chlorophyll relaxation dynamics. We extended our structure-based model of the PSII supercomplex to membranes with differing ratios of PSII to LHCII, differing spatial segregations of PSII and LHCII and differing degrees of LHCII aggregation.

Fundamental Mechanisms for Solar Energy Conversion in Photosynthesis and Photosynthetic Hybrid Systems

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Funding: \$856,000 (2014)

PROGRAM SCOPE

Photosynthesis serves as a paradigm for solar photochemistry energy conversion within highly-tuned and chemically complex cofactor environments provided by protein frameworks. In this program photosynthetic hybrids are developed as model systems that allow fundamental mechanisms for photosynthetic energy conversion within protein environments to be investigated with a higher precision and greater variety of cofactors than can be achieved with native photosynthetic reaction center assemblies. Multiple cofactor protein 'wires' are investigated as prototype building blocks for the design of semi-synthetic architectures for solar fuels catalysis. In these concepts, the multiple cofactor

redox proteins serve as sources/sinks for electrons in fuels catalysis in hybrid assemblies constructed with photosensitizer-catalyst dyad assemblies. This program investigates fundamental processes of photosynthetic solar energy conversion that link transient, single electron excited-state on light-harvesting molecules with proton-coupled electron transfer, water oxidation and chemical energy conversion in photosynthetic protein environments. The goal of this program is to resolve fundamental mechanisms for light-harvesting and coupling of excited-state photochemistry to proton-coupled electron transfer, water oxidation, and chemical energy conversion in photosynthesis, and to test design concepts in semi-synthetic photosynthesis using photosynthetic hybrid systems. The program advances forefront time-resolved synchrotron x-ray, optical, and electron paramagnetic resonance (EPR) approaches for the resolution of fundamental mechanisms for solar energy conversion. This program will resolve fundamental mechanisms for photosynthetic solar energy conversion and provide concepts for the design of efficient natural and artificial photosynthetic systems based on biological host-guest chemistry with sustainable atomic compositions.

FY 2014 HIGHLIGHTS

This program investigated multi-heme cytochrome c7 'molecular wires' from *Geobacter sulfurreducens* as prototype frameworks for construction of semi-synthetic reaction center mimics for solar fuels catalysis. Strategies for introducing light harvesting and catalyst cofactors were investigated using the tri-heme domain, PpcA. Molecular recognition and electrostatic surface docking were investigated from NMR chemical shift perturbation measurements using anthraquinone-2,6-disulfonate (AQDS) as an electron donor substrate. The measurements found that the region around the PpcA heme IV interacts with AQDS through the formation of a reversible electron transfer complex with a K_d of 18 mM (BBA 2014, 1837: 750). The result identified a likely physiological entry point and pathway for intramolecular electron transfer in PpcA. Companion molecular recognition studies using tetrasulfonated porphyrins as anionic photosensitizers for electrostatic docking to the cationic PpcA was investigated using fluorescence quenching, small angle X-ray scattering, and all-atom molecular dynamics simulations (Biochem. 2014, 53: 5070). The results found that tetrasubstituted charged porphyrins serve as bridging ligands nucleating dimerization of the complementarily charged PpcA with sub-millimolar disassociation constants, while extensive multimerization beyond dimers were found for cyt. c and lysozyme cationic proteins. Models of the aggregation products suggest that multimerization involves a combination of electrostatic and hydrophobic interactions and demonstrate an overlooked complexity in the design of multifunctional ligands for protein surface recognition. Multimerization that self-limits to a dimer for PpcA is consistent with an association mechanism driven by a single ligand binding site on the protein surface. Cobaloxime catalyst incorporation via histidine coordination in heme deleted sites was investigated using myoglobin as a protein model (Inorg. Chem. 2014, 53: 8071).

Energy Conversion in Photosynthesis - Mechanism of Water Oxidation and Oxygen Evolution

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Funding:	\$991,000 (2014)

PROGRAM SCOPE

The objective of this proposal is to understand the mechanism by which water is oxidized to dioxygen at the Mn_4CaO_5 site. We propose to develop and utilize new methodologies of X-ray spectroscopy and crystallography in our investigations of photosynthetic water oxidation. The specific questions that are our focus and of the new methods being developed are: 1) What are the geometric and electronic structural changes of the Mn_4CaO_5 cluster of the photosynthetic OEC of Photosystem II? 2) How do the protein environment and the catalytic center interact with each other to carry out the sequential events during the four-electron water oxidation reaction, under ambient conditions? 3) Application of X-ray spectroscopic techniques to artificial photosynthetic systems. The present knowledge of the water oxidation reaction was accumulated primarily by studying cryo-trapped states with crystallography and various spectroscopic techniques. The question arises whether the information can be directly translated to the reaction that occurs under ambient conditions. More importantly, how the O-O bond formation, successive water substrate binding, and a rearrangement of the OEC occur through transient states between the S_3 to S_0 states? We plan to combine SR-based X-ray techniques and XFEL techniques to tackle these questions. A substantial part of this proposal is built upon our on-going development at XFEL facilities. While a large part of the current XFEL research is on crystallography, we also focus on the development of spectroscopic techniques for a seamless understanding of overall protein dynamics and chemical changes at the catalytic site; how the protein environment modulates the site for the catalytic reaction to occur through sequential events of photo-absorption, and electron and proton transfer reactions. We note that the methods we propose here will also be applicable to artificial photosynthesis research and catalysis research in general.

FY 2014 HIGHLIGHTS

Simultaneous Femtosecond X-ray Spectroscopy and Diffraction of Photosystem II at Room Temperature: The XES/XRD of PSII in various illuminated states was collected. We collected XES from PS II for the S_3 , S_0 and one intermediate time point at 250 μs in the transition between S_3 and S_0 , showing that the data for S_3 and S_0 match with previous data measured under cryogenic conditions at synchrotron sources and confirming that PS II is advanced through its catalytic cycle with our experimental conditions. In addition the XES signal measured at 250 μs after the S_3 state formation shows that within the 250 μs after the light excitation, no Mn-reduction has yet taken place, indicating that the peroxo-bond is not formed within this interval. We also collected XRD in the S_3 , S_0 and the time point of 250 μs after S_3 . The best spots were observed up to 4 \AA and complete datasets to $\sim 4.5\text{-}5.1$ \AA were obtained for each S-state. A strong anomalous signal from Mn was observed with its maximum centered in the middle of the Mn_4Ca cluster for all of the flash/S-states measured. The Ca atom is not within this density as expected. The result was published in Nature Comm 2014 (DOI: 10.1038/ncomms5371).

Physical Biosciences

Institutions Receiving Grants

Hyperthermophilic Multiprotein Complexes and Pathways for Energy Conservation and Catalysis

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

We are investigating the properties of energy transducing systems, the processes that regulate energy-relevant chemical reactions, the architecture of biopolymers, and the active site protein chemistry leading to efficient bio-inspired catalysts. The protein complexes under study have the remarkable property of being synthesized (self-assembling) at temperatures near 100°C in hyperthermophilic microorganisms. The complexes are involved in the conversion of low potential reducing equivalents into gaseous end products with the concomitant conservation of energy in the form of ion gradients. The model microorganism is *Pyrococcus furiosus* (Pf), which grows optimally at 100°C. Pf obtains energy for growth by fermenting carbohydrates and producing hydrogen gas and by reducing elemental sulfur (S°) to hydrogen sulfide. It has a respiratory metabolism in which it couples hydrogen gas production by a membrane-bound hydrogenase (MBH) to formation of a membrane potential that Pf utilizes to synthesize ATP. Pf also contains a cytoplasmic hydrogenase (SHI) that has the rare property of evolving hydrogen from NADPH, a reaction of utility in hydrogen production systems. Addition of S° to Pf prevents the synthesis of MBH and SHI, and induces synthesis of a membrane complex termed MBX. MBX is highly similar to MBH but is proposed to reduce S° and conserve energy by an as yet unknown mechanism. The specific aims of the proposed research are to characterize SHI, MBH, MBX and related respiratory complexes. The results of this research will provide a fundamental understanding of how the production of hydrogen sulfide and hydrogen lead to energy conservation. The goals will be achieved utilizing up to 800-liter fermentations of Pf, large-scale anaerobic enzyme purifications of cytoplasmic and membrane complexes, and various biochemical, genetic, spectroscopic and structural approaches.

FY 2014 HIGHLIGHTS

We have taken advantage of the recently developed genetic system in Pf to over-express an affinity-tagged version of SHI that can be purified by a one-step procedure. The pure protein has been used in *in vitro* enzyme pathways to produce H₂ and in collaborative studies for direct electrochemical and spectroscopic (FTIR) analyses. An affinity tagged-version of MBH was solubilized and purified from Pf membranes and was biochemically characterized. In a collaborative study the structural envelope of the soluble MBH complex was determined using small-angle X-ray scattering (SAXS). An extensive phylogenetic and bioinformatic analysis of MBH and MBX revealed that they are modular in nature and represent ancestral respiratory complexes. Two hyperthermophilic membrane complexes termed formate hydrogen lyase (encoded by 18 genes) and carbon monoxide dehydrogenase (16 genes) are closely-related to MBH and contain additional formate- and carbon monoxide-oxidizing modules. The

operons encoding these two complexes were each successfully expressed in Pf and these enabled the organism to convert formate or carbon monoxide to hydrogen gas and to use carbon monoxide as a source of energy for growth. In addition, by differential expression of the 14 genes within the operon encoding Pf MBH, an affinity-tagged, catalytically-active and soluble sub-complex of the enzyme containing five proteins was purified from Pf and biochemically-characterized.

Cellulose and the Control of Growth Anisotropy

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Funding: \$170,000 (2014)

PROGRAM SCOPE

Plant cell walls are tough and strong, characteristics that give plants mechanical integrity and give humanity durable and flexible wood and fiber. Cell walls owe much of their strength to cellulose microfibrils, long crystalline polymers of glucose, with strength rivaling steel. In a growing cell, microfibril strength, alignment, and interactions with the cell wall matrix allow expansion to be controlled, a control that is exerted not only on rate but also on direction. Expansion is anisotropic, and plants must control this anisotropy precisely to build organs with specific and functional shapes, i.e., for morphogenesis. Overall, this project aims to understand how the cell aligns cellulose microfibrils and how aligned microfibrils dictate the anisotropy of growth. The project uses the emerging model plant, *Brachypodium distachyon*. The objectives are to 1) Isolate and characterize root morphology mutants in *B. distachyon*; 2) Characterize variability in *B. distachyon* accessions for root morphology and cellulose synthesis rate; 3) Use reverse-genetic approaches to study the function of *B. distachyon* genes suspected to be important in cellulose synthesis; and 4) Develop methods for scanning electron microscopy to characterize cell wall architecture. The project uses a grass, a family of plants that have long sustained humanity with their nutritious seed and might soon be sustaining us as a source of liquid fuel. Grasses have a different kind of cell wall than other angiosperms, and one whose assembly is poorly understood. Recent research on grasses applies almost exclusively to the secondary cell wall; however, primary cell walls are responsible for the growth and shape of the plant body. Focusing on the primary cell wall, the results should increase our ability to understand and hence to optimally modify plant growth.

FY 2014 HIGHLIGHTS

We continue to verify phenotypes and inheritance of various morphological mutants pulled out of the forward genetic screen in *B. distachyon* and we have confirmed the existence of a mutant that initiates and fails to elongate root hairs. We have characterized root growth in *B. distachyon* using high resolution kinematics and conducted pilot runs to determine whether this can be used in a genome-wide association study to characterize the genetic structure of growth components. We have obtained an insertional mutant in one of the *B. distachyon* genes that synthesize cellulose for the primary cell wall. Currently, we are determining whether this can be fully complemented by the wild type gene, with or without a fluorescent protein tag. We have shown that, as a reverse genetics approach, gene silencing using hairpin constructs expressed constitutively fails because effects at the callus stage are

too severe for plant regeneration. As a consequence, we have placed silencing constructs under the control of an inducible promoter and these are currently being evaluated for expression and regeneration. Finally, for our high resolution studies of cell wall structure with scanning electron microscopy, we have shown that freeze drying from tert-butanol is a useful method and we succeeded in developing a protocol to identify specific structures with immuno-gold labeling. This method will be indispensable for understanding cell wall structure above the single polymer level.

Role of HydF in Hydrogenase Maturation

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Funding: \$170,000 (2014)

PROGRAM SCOPE

The goal of the project is to elucidate the biosynthetic pathway for the [FeFe]-hydrogenase active site metallocluster, the H-cluster. The potential for harnessing biological hydrogen production as an energy solution cannot be fully realized without a complete fundamental understanding of how the complex metal clusters at the active sites of hydrogenases function and are synthesized. The hydrogenase H-cluster is an unusual iron-sulfur cluster assembly which exists as a [4Fe-4S] cluster cubane bridged to a 2-Fe cluster containing multiple inorganic (CO and CN⁻) ligands as well as an exogenous bridging dithiolate ligand. Three gene products, HydE, HydF, and HydG, have been implicated in the assembly and maturation of functional hydrogenase (HydA). Based on sequence analysis, two of these proteins (HydE and HydG) belong to the radical-SAM superfamily, proteins that utilize S-adenosylmethionine and a [4Fe-4S] cluster to initiate radical chemistry. The third (HydF) is a GTPase. Thus, assembly of the complex H-cluster of hydrogenase requires unique assembly machinery that is distinct from the standard host cell machinery like the Isc proteins involved in assembly of “standard” [2Fe-2S] and [4Fe-4S] clusters. Our research implicates HydF as a scaffold upon which the two radical SAM enzymes HydE and HydG act to synthesize and insert the unique non protein ligands through the modification of a [2Fe-2S] cluster precursor. The goals of this project are to develop a molecular-level understanding of the reactions catalyzed by HydE, HydF, and HydG by exploiting our preliminary results and using the HydF scaffold as a means to capture and characterize cluster synthesis intermediates. This work will reveal fundamentally unique biochemistry and help define valuable paradigms for complex metal cluster assembly in biology.

FY 2014 HIGHLIGHTS

We have made extensive progress in understanding the mechanism of HydG, and the roles of the two iron-sulfur clusters of HydG in this mechanism, as detailed in two publications during FY2014. We have shown that the N-terminal iron-sulfur cluster alone is required for reductive cleavage of SAM and subsequent tyrosine cleavage to produce p-cresol. The C-terminal iron-sulfur cluster is required for subsequent conversion of a tyrosine-derived intermediate to cyanide and CO. We have also shown that the H-atom abstraction initiated by HydG is a reversible process, with abstraction occurring at a solvent-exchangeable site. In our studies of HydE, we have utilized biochemical and bioinformatics approaches to provide considerable insight into the catalytic reaction catalyzed by HydE; we currently have a

manuscript in revision describing these results. In our efforts to characterize the scaffold HydF, we have employed spectroscopic and biochemical techniques to provide evidence for the active oligomeric state of HydF, and to demonstrate how the iron-sulfur cluster states of HydF vary with the oligomeric state of the protein. We have also successfully expressed *Thermatoga* HydF in a thermophilic *P. furiosus* host, and have used FTIR to demonstrate that this HydF contains the CO and cyanide ligands characteristic of the “loaded” form of the HydF scaffold.

The Role of Carbonic Anhydrase in C(4) Photosynthesis

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Funding: \$57,120 (2014)

PROGRAM SCOPE

Current pressures on the global food supply have accelerated the urgency for a second green revolution using novel and sustainable approaches to increase crop yield and efficiency. This proposal outlines experiments to address fundamental questions regarding the biology of C₄ photosynthesis, the method of carbon fixation utilized by the most productive food, feed and bioenergy crops. Carbonic anhydrase (CA) has been implicated in multiple cellular functions including nitrogen metabolism, water use efficiency, and photosynthesis. CA catalyzes the first dedicated step in C₄ photosynthesis, the hydration of CO₂ into bicarbonate, and is potentially rate limiting in C₄ grasses. Using insertional mutagenesis, we have generated CA mutants in maize, and propose the characterization of these mutants using phenotypic, physiological, and transcriptomic profiling to assay the plant’s response to altered CA activity. In addition, fluorescent protein tagging experiments will be employed to study the subcellular localization of CA paralogs, providing critical data for modeling carbon fixation in C₄ plants. Finally, I propose parallel experiments in *Setaria viridis* to explore its relevance as model C₄ grass. Using a multifaceted approach, this proposal addresses important questions in basic biology, as well as the need for translation research in response to looming global food challenges.

FY 2014 HIGHLIGHTS

An evolutionary genetics approach to studying C₄ photosynthesis relies on comparisons to C₃ species. Rice and brachypodium (members of the BEP clade) are the C₃ species currently used for comparisons with C₄ panicoid grasses such as maize, sorghum, setaria, switchgrass, and sugarcane, which are important for both biofuel and food production. The most recent common ancestor of these C₃ and C₄ grasses lived ~52 million years ago. Thus, there is a need to sequence a C₃ panicoid grass, which would give comparative studies more power to detect changes related to the evolution of C₄ photosynthesis. In an effort to identify a more informative C₃ species for evolutionary comparison, I initiated a collaboration with Dr. Elizabeth Kellogg. We identified *Dichanthelium oligoanthes* as a superior C₃ grass comparator because it shared a common ancestor with maize ~26 million years ago and it has a relatively small diploid genome of ~900 Mb. In addition, it has sister taxa that have evolved all three subtypes of C₄ photosynthesis, which indicates that *D. oligoanthes* might contain intermediate mutations on the evolutionary path to C₄ photosynthesis. Research funds from this fellowship have advanced this project, and currently we have a draft genome assembly (done in collaboration with Dr. James

Schnable). The genome of *D. oligoanthes* will not only provide a better C₃ in-group for comparisons with C₄ grasses, but it also will be a resource for the grass community as another model grass species. This work has also provided a proof of concept for a JGI funded CSP grant to sequence other grass transcriptomes. JGI has also agreed to do additional sequencing to improve the assembly of *D. oligoanthes*.

Jasmonate Hormone: Regulating Synthesis of Reduced Carbon Compounds in Plants

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Funding: \$170,000 (2014)

PROGRAM SCOPE

Our original interest in understanding the role of jasmonate (JA) in regulating the final stages of stamen and pollen development led to our discovery of the JAZ repressors, and the molecular mechanism of JA action is now a second important focus of our research. The specific goals for this grant period are to:

1. Investigate the generation and clearance of the hormone with emphasis on the regulation of the OPR3 enzyme and the hydrolysis of JA-Ile.
2. Use dominant-negative and overexpression constructs to explore the role of the MYC5 transcription factor in initiating and regulating JA responses.
3. Investigate specific JAZ protein interactions that will help us to recognize and understand the extended network of processes, such as sulfur nutrition, that interface with JA signaling.

FY 2014 HIGHLIGHTS

The COI1 F-Box protein is a JA-Ile coreceptor and *coi1* mutant plants lack JA responses. We have tested the possibility that sites of JA action can be probed by using tissue-specific promoters to drive expression of a COI1-YFP fusion protein in *coi1* mutant plants deficient in stamen and pollen function. When we expressed COI1 behind a filament-specific promoter (from the DAD1 gene), filament elongation was restored but not anther dehiscence or pollen function. Three tapetum specific promoters, all failed to restore any of these three functions but, unexpectedly, a promoter active in the stomium and epidermal cells, restored both pollen function and anther dehiscence. Most importantly, our results demonstrate the power of promoter::COI1-YFP constructs in revealing the primary sites of JA-regulated gene expression that control developmental and other responses in neighboring tissues. We now plan to use this new tool to test current hypotheses about JA action in other organs of the plant. The MYC2, MYC3, and MYC4 proteins are the primary transcription factors initiating defense and root growth responses to JA signaling. However, transgenic plants overexpressing these proteins do not show any substantial reduction in shoot growth, even though they have increased expression of many JA-responsive genes. MYC5 is closely related to MYC2, MYC3, and MYC4 but has not previously been considered a candidate in JA signaling, in part because *myc5* mutants exhibit no overt phenotype. However, when we overexpressed the MYC5 protein in wild-type *Arabidopsis* we got a surprising result. Whereas plants overexpressing MYC2 were similar in size to wild type, as observed previously, MYC5-OE plants were much smaller. This is an exciting discovery because it indicates that growth responses to JA

may be controlled by a signaling pathway that is distinct from that pathway (or pathways) controlling secondary-product synthesis and defense.

N-Acylethanolamine metabolism and the acquisition of photoautotrophy during seedling establishment

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Funding: \$360,000 (2014-2015)

PROGRAM SCOPE

Research in our labs has led to the discovery of a new lipid mediator pathway that influences phytohormone-mediated regulation of plant growth and development—the so-called N-acylethanolamine (NAE) regulatory pathway. This pathway in plants shares conserved metabolic machinery with the endocannabinoid signaling system of vertebrates that regulates a multitude of physiological and behavioral processes in mammals, suggesting that the metabolism of NAEs is an important regulatory feature of eukaryotic biology. Current evidence in plants points to interactions between NAE metabolism, abscisic acid (ABA) signaling and light signaling to modulate seedling establishment and the acquisition of photoautotrophic growth. Our main hypothesis is that seedlings coordinate the metabolic depletion of NAEs during seedling establishment through a complex interaction of hydrolysis (by fatty acid amide hydrolase, FAAH) and oxidation (by lipoxygenases, LOX) and that oxylipin metabolites of polyunsaturated NAEs help to coordinate seedling development and acquisition of photoautotrophy in response to appropriate environmental cues. Evidence suggests that ethanolamide oxylipins derived from NAEs can reversibly accumulate in seedlings and adjust/arrest seedling establishment and chloroplast development in conjunction with ABA signaling and light-signaling pathways. Three specific aims are proposed to elucidate the molecular details of the NAE regulatory pathway and further test our hypothesis: 1) Uncover mechanisms by which NAEs control seedling establishment by mutant analysis and chemical genetics, 2) Identify molecular targets of ethanolamide oxylipins specifically derived from NAE18:3 and NAE18:2, 3) Evaluate spatial factors (tissue/ cellular) important in the regulation of seedling establishment by ethanolamide oxylipins. We anticipate that results from our proposed studies will provide important new information linking the production

FY 2014 HIGHLIGHTS

Analytical methodology was developed to allow for the identification and quantification of two important and unknown metabolite pools—the N-acylphosphatidylethanolamines (precursors of NAEs) and the oxylipin metabolites of polyunsaturated NAEs. These technological advances facilitated the discovery and description of NAE metabolism during seedling establishment with unprecedented detail. Further, they have provided a new appreciation for the bioactivity of lipoxygenase-derived NAE metabolites, and have supported a bifurcating, complex action of NAEs with some species affecting only chloroplast assembly and others regulating root elongation. Transcriptional profiling suggests the involvement of both ABA and light signaling pathways in the action of NAE oxylipins. These results were published in part in Keereetaweep *et al.*, (2013; *Plant Cell*, 25:3824-40), and featured in an “In-Brief” summary article by Nancy Hoffmann (Ethanolamide Oxylipins: New Players in Seedling Development,

Plant Cell, 2013, 25: 3637). Recent attention to acylethanolamides as important regulatory molecules in plants is evidenced by a recent review published in a special issue on small molecule signaling in the Plant Journal (Blancaflor *et al.*, 2014, 79:568-83) and featured as part of the cover art on the Aug 2014 issue.

Regulation of Carbon Allocation to Phenylpropanoid Metabolism

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

The goal of this project is to understand the mechanisms that plants use to determine how much photosynthate is funneled into the phenylpropanoid metabolic pathway, the most abundant product of which is the phenolic cell wall polymer lignin. Consistent with the enormous commitment of energy and carbon it requires, the synthesis of lignin is under tight regulatory control. The picture emerging from recent work is that this control is effected by a complex, hierarchically organized network of transcription factors, many of them MYB and NAC domain-containing proteins, in which proteins near the top of the regulatory cascade act to regulate the expression of other transcription factors, while those located at the most downstream points in the network regulate the transcription of the phenylpropanoid biosynthetic enzymes directly. We have determined that the transcriptional co-regulatory complex Mediator plays an important role in integrating the input from these transcription factors into a coordinated transcriptional response. In particular the Med5 subunit of the complex is required for normal phenylpropanoid homeostasis. We have identified two previously uncharacterized components of the Mediator complex, REF4 and RFR1 that negatively influences the accumulation of phenylpropanoid metabolites. To gain more insight into the biological roles of REF4 and RFR1 and the influence of phenylpropanoid metabolism on plant growth and morphology, we will (1) determine the components found in REF4- and RFR1-containing Mediator complexes, (2) identify the specific regions in the genome to which REF4- and RFR1-containing Mediator complexes are targeted, and (3) determine whether there are functional differences between REF4 and RFR1. By completing this set of experiments, we will learn how REF4 and RFR1 function to coordinate transcription of genes required for lignin deposition and gain insights into how this pathway can be manipulated for human energy needs.

FY 2014 HIGHLIGHTS

We have found that the phenotype of the lignin-deficient *Arabidopsis ref8* mutant is dependent on an intact Mediator complex. Disruption of the genes encoding the Med5 subunits in a mutant blocked early in the pathway rescues not only its growth, but also its ability to synthesize wild-type levels of lignin. Cell walls of the rescued plant contain almost exclusively p-hydroxyphenyl lignin subunits and exhibit substantially facilitated polysaccharide extraction. These results implicate Mediator in an active process that causes dwarfing and inhibition of lignin biosynthesis. RNAseq experiments using Med5 mutants and Med5-deficient *ref8* plants indicated a fairly specific role for Med5 in the regulation of phenylpropanoid metabolism and a dramatic reprogramming of transcription in *ref8* when Med5 function was eliminated,

with over 90% of the genes mis-regulated in *ref8* no longer misregulated in *med5 ref8*. We have identified mutations in other Mediator tail subunits that appear to be important for REF4 function. We have completed soluble metabolite and lignin analysis on these lines and have found that some accumulate wild-type levels of sinapoylmalate, while others accumulate less than wild-type plants. We also found that disrupting one of these Mediator genes significantly rescues the growth of the lignin-deficient *ref8* mutant described above, although not to the same degree as did disrupting Med5. These results indicate that multiple Mediator tail subunits may be involved in repression of the phenylpropanoid pathway. We have also had significant recent success in generating molecular reagents that will be required to address many of our original research goals. We have generated a high avidity anti-Med2 antibody for use in chromatin immunoprecipitation experiments and have succeeded in expressing Med2, Med3, and Med5 in the baculovirus expression system. These additional proteins will be used for antibody production and will also be put into crystallization trials.

Asparagine Synthetase Gene Regulatory Network and Plant Nitrogen Metabolism

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

This project concerns the regulatory mechanisms by which plants coordinate C, N, and energy use efficiency. We focus on mechanisms that regulate the most energy-intensive biochemical pathway in plants - assimilation of inorganic nitrogen onto C-skeletons. Specifically, inorganic N initially assimilated into reactive Gln (C₅:N₂) is converted into inert Asn (C₄:N₂), a more C-efficient amino acid used for CN-storage/transport under low energy states. Using a genetic screen, we discovered a master gene encoding a histone methyltransferase (SDG8) that mediates genome-wide responses to low energy/C sensing by coordinating expression of genes involved in photosynthesis, energy generation and C/N-metabolism. We studied how changes in chromatin, transcription, and metabolite signaling mediate genome-wide responses to changes in C and energy availability.

In Aim 1, we determined how histone methylation by SDG8 affected expression of genome-wide targets using three measures: i) SDG8-target binding, ii) H3K36 trimethylation and iii) Gene expression. Remarkably, >50% of the 728 high-confidence SDG8 targets are light-regulated genes that span energy generation and energy utilization. We also uncovered conserved cis-motifs in these SDG8 targets whose associated proteins are implicated in light-regulation.

In Aim 2, we explored how epigenetic targets of SDG8 lead to changes in expression of a network of downstream genes. We showed that GLK1, a target of SDG8, is a master regulator of genes involved in energy generation and use.

In Aim 3, we validated that signaling by N metabolites is affected via histone methylation of H₃K4 residues in target genes of SDG8. Our results support a model where SDG8 specifically targets the methylation of histones associated with genes involved in energy capture, conversion and use. This is the first implication of the histone code as a mechanism that enables plants to coordinate genome-wide responses to fluctuations in energy and metabolic state.

FY 2014 HIGHLIGHTS

Aim 1: Using Gene-chip mapping and complementation, we showed that the *sdg8-5* mutant defective in C and L regulation of *ASN1* carries a complete deletion of *SDG8*, a gene encoding a H3K36 methyltransferase. We determined the genome-wide targets of *SDG8* and how this histone methylation by *SDG8* affected expression of its targets by probing the targets of *SDG8* using 3 methods: i) *SDG8*-binding, ii) H3K36 trimethylation, iii) Gene expression. Remarkably, >50% of the 728 high-confidence direct targets of *SDG8* are light-regulated genes that span energy generation and utilization. We showed that the H3K36me3 marks on histones associated with *SDG8* target genes correlate with elevated levels of mRNA expression that is disrupted in the *sdg8-5* mutant. Finally, we uncovered conserved cis-motifs in the promoters of the *SDG8* targets: G-box and FORCA motif, a light- and defense- integrator motif whose associated proteins are implicated in light-regulation.

Aim 2: We validated that *ASN1* is a target of *GLK1* using an over-expresser and a *glk1/glk2* double mutant. We also identified global targets of *GLK1* using the TARGET system. Among the 196 identified *GLK1* direct target genes, GO-terms like photosynthesis, chlorophyll binding, and light-harvesting complex are significantly over-represented, confirming and extending the reported roles for *GLK1*. A significant overlap was observed between the 196 *GLK1* targets and the 728 *SDG8* targets, indicating that the H3K36me3 histone modification of ~13% of *GLK1* targets are dependent on *SDG8*. These studies show that *GLK1* is a master regulator of genes involved in energy generation and use.

Aim 3: To study how H3K36 methylation by *SDG8* affects plant responses to N- signals we assayed the global H3K36me3 profiles by CHIP-seq of plants treated with a 5 hr inorganic N-treatment, comparing the *sdg8-5* mutant to wt. Our preliminary results indicate that the *sdg8-5* mutant shows an impaired epigenetic response to the supply of N-nutrient signals.

Molecular Mechanisms of Plant Cell Wall Loosening

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Funding: \$475,000 (2014-2016)

PROGRAM SCOPE

We are studying the biophysical and molecular bases of plant cell wall loosening, which is essential for plant cell growth and is connected to many plant developmental processes, to plant defense, and to new technologies for engineering plant growth and for bioconversion of cell walls into useful materials and sustainable biofuels as a substitute for fossil fuels. Our current focus is on the molecular interactions of expansin proteins with plant cell wall polymers, with the aim of understanding how expansins modify wall polymer interactions and structures in the growing cell wall, resulting in physical effects such as wall stress relaxation, polymer creep, and increase in surface area of the cell wall. This is significant for an understanding of the molecular basis of plant cell growth and for a molecular understanding of important physical properties of plant cell walls such as strength, rheology, extensibility, anisotropy, enzyme accessibility and recalcitrance to physical treatments and biochemical conversion to simpler molecules. In this project we have discovered three groups of expansins: plants have α - and β -expansins (EXPA and EXPB), and some bacteria have expansins (EXLX) as well. Expansins do not have wall lytic activity, yet they induce wall relaxation and cell wall creep. Their mechanism is enigmatic in part

because our understanding of cell wall structure is woefully incomplete. We have made use of bacterial expansins for structure/function analyses by X-ray crystallography and site-directed mutagenesis combined with binding assays, wall creep assays and dynamic mechanical analyses of cell walls. We are also pioneering the use of sensitivity-enhanced solid-state NMR to identify the target of bacterial and plant expansins (a collaboration with Dr. Mei Hong, MIT).

FY 2014 HIGHLIGHTS

1. Elucidated the mechanism of glycan binding by the expansin (BsEXLX1) from *Bacillus subtilis*. This involved solving the structure of multiple protein:ligand complexes as well as use of site-directed mutagenesis and a variety of activity assays. In the crystal the protein:ligand packs in an exceptional configuration in which two proteins bind to a single ligand, with the proteins in opposite orientation and staggered register on the opposite sides of the ligand. This work also established expansin domain 2 (the C-terminal domain) as the founding member of Carbohydrate Binding Module family 63 (CBM63 in the CaZy database). Moreover we found that BsEXLX1 binding to whole cell walls was complex: the majority of binding was relatively nonspecific binding to pectins, driven by electrostatic interactions, and was nonproductive (meaning it reduced wall loosening activity of the protein); whereas the productive binding was between a β 1,4-glucan chain and a set of three aromatic residues set in line on the surface of domain 2.
2. We characterized the molecular target of the expansin BsEXLX1 by use of sensitivity-enhanced solid-state NMR in combination with a variety of site-directed mutants and C_{13}/N_{15} labeling. This was a collaboration with Dr. Mei Hong (currently at MIT). The result shows that expansin binds to cellulose with a conformation somewhat different (less organized) than that of bulk cellulose and that xyloglucan is in close proximity.
3. Discovered that maize EXPB1 dissolves the middle lamella of growing maize coleoptiles and facilitates separation of the cuticle from the epidermal cell walls. Biochemical mechanism is uncertain.

Center for Plant and Microbial Complex Carbohydrates

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Funding: \$850,000 (2014)

PROGRAM SCOPE

The Complex Carbohydrate Research Center (CCRC) of the University of Georgia is a national resource for the study of complex carbohydrates. The DOE Center enables the CCRC to provide services and training to academic, government, and industrial researchers who study the complex carbohydrates of plants and microbes by providing support of experts who operate, maintain, and assist in interpreting the data obtained from a variety of scientific instrumentation. The expanding need for expertise in studies of the structure/function of complex carbohydrates is rapidly growing as the importance of carbohydrate research in areas such as biomass conversion to biofuels and biomaterials is being recognized. The DOE Center enables several types of service to be offered to researchers. Scientists who request analytical service(s) receive a written report containing a description of the analytical

procedures used, publishable quality results (data), and an authoritative interpretation of the results. Personnel also provide collaborative service by becoming involved in “in depth” research projects with individuals from other laboratories. One hallmark of the service offered is the continued addition of new technologies originally developed within the CCRC. The DOE Center also provides researchers with often hard to obtain chemical and biological samples, including monoclonal antibodies specific for plant cell wall epitopes and nucleotide sugars for biosynthetic studies. Training students and scientists in various fields of carbohydrate science is a very important part of the Center’s mission. Training occurs when undergraduates, graduate students, postdoctoral fellows, and visiting scientists undertake research projects with or take formal courses from faculty and staff. In addition, several annual one-week training courses and one- and/or two-day specialized courses are offered for individuals from academic, industrial and government institutions.

FY 2014 HIGHLIGHTS

The DOE Center of the University of Georgia is a national resource for the study of complex carbohydrates. The DOE Center provides services and training to academic, government, and industrial researchers by supporting experts who operate, maintain, and assist in interpreting the data from a variety of scientific instrumentation. The expanding need for expertise in studies of the structure/function of complex carbohydrates is rapidly growing as the importance of carbohydrate research in areas such as biomass conversion to biofuels and biomaterials is being recognized. The DOE Center provides several 'high demand' analytical services to the scientific community, including (1) purification and analysis of plant and microbial polysaccharides; (2) isolation and characterization of plant and microbial glycoproteins; (3) molecular weight determination by SEC, MALDI-MS, or ESI-MS; (4) glycosyl composition analysis; (5) glycosyl linkage analysis; (6) determination of absolute configuration; (7) structural elucidation by ESI-MS and ESI-MS/MS, MALDI-MS and LC-ESI-MS/MS; (8) 1-D and 2-D NMR; (9) lignin and tannin analysis using Py-MBMS and Py-GC-MS; (10) CarboSource Services: production of rare nucleotide-sugars, acceptors for glycoconjugate biosynthesis, and of monoclonal antibodies reactive against plant cell wall epitopes; and (11) glycome profiling. In 2014, 1174 total analyses were performed on 600 samples. Training students and scientists in glycoscience is an important part of the DOE Center’s mission. Training occurs when undergraduate and graduate students, postdoctoral fellows, and visiting scientists undertake research projects or take formal courses from faculty and staff. In addition, several annual hands-on one week or two or three day specialized courses are offered to individuals from academia, government laboratories, and private industry. In 2014, 48 individuals from academic institutions and industry participated in these specialized courses.

Mechanistic Studies of Catalysis in Quinone Electron Transfer Using High-Resolution EPR

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

Our goal is on use of pulsed EPR spectroscopy to explore the catalytic domains trapped in states with semiquinone (SQ) as an intermediate. The catalytic sites we propose to study– the Q_A and Q_B sites of the

reaction center, the Q_i site of the bc₁ complex, and the Q_H site of the bo₃ quinol oxidase – all operate using ubiquinone, but have different electron transfer partners and different operating potentials. EPR probes interactions between the electron spin of SQ and local magnetic nuclei, which provide direct information about spatial and electronic structure of the SQ and the immediate protein and solvent environment. The main question to be addressed is that of how the protein environment modifies the spatial and electronic structure of the SQ in different sites to fit the physiological function.

FY 2014 HIGHLIGHTS

The 2-methoxy group generates a redox potential difference between SQ_A and SQ_B. Only quinones with a 2-methoxy group can act simultaneously as the Q_A and Q_B ubiquinone (UQ) electron acceptors in photosynthetic reaction centers from *Rb. sphaeroides*. ¹³C pulsed EPR measurements of 2-methoxy in the SQ_A and SQ_B states were compared with the ¹³C hyperfine (hfi) couplings calculated as a function of dihedral angle. X-ray structures support dihedral angle assignments corresponding to a redox potential gap between Q_A and Q_B of >160 mV. This is consistent with the failure of a UQ analog lacking the 2-methoxy to function as Q_B in wild type ($\Delta E_m \approx 60-75$ mV) and mutant ($\Delta E_m \approx 160-195$ mV) reaction centers. Auxotrophic strains for specific labeling in *Rb. sphaeroides*. A methionine (Met) auxotroph of *Rb. sphaeroides* has been generated by replacing the *metA* gene in the chromosome with a *cat* gene that provides chloramphenicol resistance. ¹³C isotopic labeling of the -CH₃ and CH₃O- substituents of UQ₁₀, was achieved using this Met auxotroph in *Rb. sphaeroides* strain BC17, supplemented with [methyl ¹³C] L-methionine, with the bc₁ complex expressed from a plasmid-borne *fbc* operon. 2D ESEEM was applied to study the ¹³C CH₃ and CH₃O hfi couplings in the SQ_i generated *in situ* in the bc₁ complex. A similar protocol will be extended to generation of auxotrophic strains for other amino acids or metabolites essential in biosynthesis of prosthetic groups ¹³C tensors of the ring carbons. The anion radicals of UQ₁₀ ¹³C chemically labeled at the CH₃O-C ring positions in alcohol have been studied by 2D ESEEM to define the hfi tensors with the ¹³C nuclei. The 2D spectra allowed us to conclude that the tensors are characterized by an anisotropic component T ~ 6 MHz and an isotropic coupling a ~ -3 MHz with support from DFT calculations. The results of this work form a basis for further studies of the SQs in the protein quinone sites using ¹³C-labeling of the ring carbons.

Tuning Directionality for CO₂ Reduction in the Oxo-Acid:Ferredoxin Superfamily

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Funding:	\$360,000 (2014-2015)

PROGRAM SCOPE

Developing catalytic chemistry for bioenergy production requires a detailed understanding of the molecular mechanisms of multi-electron redox processes, particularly those that transform/capture CO₂, producing molecules useful as fuel sources or chemical feedstocks. Understanding the molecular details of how multi-electron catalysis can be achieved is a major challenge in modern energy science, particularly in the context of CO₂ transformations. While synthetic chemistry addresses the design and implementation of multi-electron transformations through the generation of homogenous or heterogenous catalysts, biological systems, such as plants and microorganisms, use diverse redox-active

enzymes to achieve CO₂ capture. Such enzymes can be highly powerful catalysts; however, very little is known about their mechanisms of action, let alone how a potential reversible catalyst can be tuned to favor CO₂ reduction chemistry. Through the completion of the project, this knowledge gap will be addressed in the context of the enzymatic chemistry of the oxo-acid:ferredoxin oxidoreductase (OFOR) superfamily, which is capable of CO₂ reduction. In this project, a series of electrochemical, structural and catalytic studies will be performed in order to ascertain the molecular details (e.g., FeS cluster redox potential) that guides the bias for reactivity in the OFOR superfamily.

FY 2014 HIGHLIGHTS

In FY2014, the project was initiated in September. Dr. Philip Steindel, a recent graduate of Brandeis University, with a background in enzymology and structural biology, was hired. Preliminary bioinformatics studies of the OFOR family has revealed further diversity in the enzymes that were previously under study, and we have expanded our efforts to the enzyme from the green sulfur microorganism *Chlorobium tepidum* and the magnetotactic bacterium *Magnetococcus sp.* MM1. Major research accomplishments thus far are that we have investigated the impact of the redox mediator upon the electrocatalytic signatures of the PFOR enzyme from *D. vulgaris*, and compared that activity to the enzyme KorAB (from *Hydrogenobacter*) which is known to be reactive in the direction of CO₂ reduction. Remarkably, we have found that while PFOR does have a latent bias toward oxidative activity, and KorAB does have a preference for CO₂ reduction (in comparison), a key feature to the development of their electrocatalytic properties is the nature of the Ferredoxin intermediary. We have found that the *Hydrogenobacter* makes use of very low potential ferredoxins ($E_m < -500$ mV) to achieve CO₂ reduction chemistry, and that the same low-potential ferredoxin can enhance the CO₂ reduction activity of a PFOR enzyme that has a preference for oxidation. The complementing case has also been demonstrated now: *D. vulgaris* possesses ferredoxins that are higher in potential ($E_m \sim -400$ mV), and these redox mediators stimulate the oxidative activity of both the native *D. vulgaris* PFOR, but also KorAB itself. The implication of this finding is that it is the nature of the redox relay system, and not the active site, that will ultimately guide the bias toward CO₂ reduction.

Extracellular Charge Transport in Microbial Redox Chains: Linking the Living and Non-Living Worlds

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Funding: \$150,000 (2014)

PROGRAM SCOPE

This project focuses on understanding the *in vivo* assembly, biophysical charge transport mechanism, and energetic consequences of extracellular redox chains that are proposed to mediate long-range (many cell-lengths) electron transport between microbial biofilms and inorganic surfaces ranging from natural environmental minerals to engineered electrodes. To gain a physics-based understanding, the research plan is designed to achieve three specific objectives:

- 1) Test whether electron transport measurements in bacterial nanowires and individual multiheme cytochromes agree with the theoretical predictions of a multistep redox hopping mechanism.

- 2) Quantify interfacial microbe-surface electron transfer at the level of single *Shewanella oneidensis* MR-1 cells, and discover how this fundamental single-cell respiration rate is impacted by the surface redox potential and selected mutations for membrane cytochromes and bacterial nanowires.
- 3) Monitor, *in situ*, the assembly of bacterial nanowires from individual cells, thereby identifying their composition, formation mechanism, and directly measure the impact of these structures on the extracellular respiration activity of live cells.

FY 2014 HIGHLIGHTS

Significant achievements (2013-2014):

- Using *in vivo* fluorescence measurements, immunolabeling, and quantitative gene expression analysis, we found that *S. oneidensis* MR-1 nanowires are extensions of the outer membrane and periplasm that include the multiheme cytochromes responsible for electron transport, rather than pilin-based structures as previously thought. These bacterial nanowires are associated with outer membrane vesicles and vesicle chains, structures ubiquitous in gram-negative bacteria. The localization of multiheme cytochromes MtrC and OmcA to these membrane extensions directly supports one of the two intensely debated models of electron transport through the nanowires (multistep hopping). We also found, for the first time, that the production of bacterial nanowires is correlated with an increase in cellular reductase activity. Paper published in the Proceedings of the National Academy of Sciences (PNAS).
- We performed scanning tunneling microscopy, single-molecule tunneling spectroscopy, and Kinetic Monte Carlo (KMC) simulations of multistep electron hopping in the multiheme cytochrome (MtrF) from the dissimilatory metal-reducer *S. oneidensis* MR-1. These are the first KMC simulations and single molecule measurements in MtrF. Paper published in ChemElectroChem.

New Perspectives on Acetate and One-Carbon Metabolism in the Methanoarchaea: Carbonic Anhydrase

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 Funding: \$70,000 (2014)

PROGRAM SCOPE

Carbonic anhydrases catalyze the reversible hydration of carbon dioxide to bicarbonate. Although widespread in prokaryotes of the domains Bacteria and Archaea, few have been investigated and the physiological functions are largely unknown. Carbonic anhydrases are of biotechnological interest for carbon dioxide capture and sequestration at point sources. Prokaryotes encode three independently evolved classes (α , β , and γ). The α -class is restricted to a few pathogens and the other two are uniformly distributed in phylogenetically and physiologically diverse species. Although wide-spread in prokaryotes, only three γ -class enzymes have been biochemically characterized and the physiological functions have not been investigated. The γ -class is prominent in anaerobic acetate-utilizing methane-producing species of the genus *Methanosarcina* that encode three subclasses. Enzymes from two of the subclasses, Cam and CamH from *Methanosarcina thermophila*, have been characterized and found to

utilize iron in the active site which is the first example of an iron-containing carbonic anhydrase. No representative of the third subclass has been isolated, although this subclass constitutes the great majority of the γ -class. This grant application proposes to characterize γ -class carbonic anhydrases from diverse anaerobic prokaryotes from the domains Bacteria and Archaea to broaden the understanding of this enzyme. In particular, the three subclasses present the genetically tractable acetate-utilizing methanogen *Methanosarcina acetivorans* will be investigated to extend studies of acetate and one-carbon metabolism in this species. A genetic approach will be taken to ascertain the physiological functions. It is also proposed to delve deeper into the mechanism of Cam from *M. thermophila*, the archetype of the γ -class, via a high resolution neutron structure and kinetic analysis of site-specific amino acid replacement variants.

FY 2014 HIGHLIGHTS

The carbonic anhydrase (Cpb) from *Clostridium perfringens* strain 13, the only carbonic anhydrase encoded in the genome, was characterized both biochemically and physiologically. Heterologously-produced and purified Cpb was shown to belong to the Type I subclass of the β class, the first β class enzyme investigated from a strictly anaerobic species of the domain Bacteria. Kinetic analyses revealed a two-step, ping-pong, zinc-hydroxide mechanism of catalysis with K_m and k_{cat}/K_m values of 3.1 mM CO₂ and $4.8 \times 10^6 \text{ s}^{-1} \text{ M}^{-1}$. Analyses of a *cpb* deletion mutant of *C. perfringens* strain HN₁₃ showed that Cpb is strictly required for growth when cultured in semi-defined medium and an atmosphere without CO₂. Growth of the mutant was the same as the parent wild-type strain when cultured in nutrient-rich media with or without CO₂ in the atmosphere, although elimination of glucose resulted in decreased production of acetate, propionate and butyrate. The results suggest a role for Cpb in anaerobic CO₂ fixation reactions by supplying bicarbonate to carboxylases.

Integration of Sugar Transport, Metabolism and Sensing in *Arabidopsis*: Optimizing Energy Efficiency in Plants - Evaluating and Targeting Leaks

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

Optimizing energy efficiency of plants: Quantitative analysis of carbon flux Crop yield and yield potential are critical for both food and feedstocks. They play key roles for feeding the planet and for the potential of biofuels to compete for oil and coal. Due to the potential for competition between each other, the yield of crops and feedstocks has to be improved in parallel. Carbon allocation is key for yield. Regulatory networks that control carbon partitioning and allocation must therefore be prime targets for optimization. Transporters control the cellular entry and release of carbohydrates in source and sink and are therefore situated in strategic positions. For efficient engineering, we need to know key players, path and bottlenecks. For this, we need quantitative spatial models using quantitative information of the sugar fluxes at the cellular and subcellular levels. To decrypt the biological circuits novel diagnostic tools are needed that, analogous to oscilloscopes in electrical engineering of circuit boards, allow quantification of fluxes, here by monitoring sugar dynamics. Such probes can provide crucial information

on systems properties. To implement impedance measurements *in vivo*, the PI's lab constructed Förster Resonance Energy Transfer sensors. Probes will be used to monitor sugar dynamics in real time. This project deploys three convergent approaches: (i) systematic analysis of SWEET function and regulation, (ii) use quantitative FRET sensor technology for identifying the cellular sugar path map, find bottlenecks, identify regulatory systems, and (iii) develop fluorescent 'transporter activity sensors' that report the activity of specific sugar transporters. These data will contribute to the development of a tissue level map and mathematical model of sugar fluxes and lay the basis for the synthetic biology to create plants with optimized carbon allocation and improved productivity.

FY 2014 HIGHLIGHTS

A bio-based economy depends critically on sufficient feedstock supplies from photosynthetic organisms. Carbon allocation in plants is therefore key to the success of such an economy, especially in the context of the competition of feedstock for food. In addition, carbon sequestration from plants can be exploited for binding atmospheric carbon dioxide. For rational engineering we need to have the knowledge of how carbon is allocated within plants and sequestered in soil. Progress in addressing the mechanistic questions of carbon allocation and sequestration can be made if suitable tools were available to monitor carbon fluxes at the subcellular level. The goal of the previous funding period was to identify novel sugar transporters and to implement fluorescent sugar sensor technology for dynamic measurements of carbon dynamics in plants. We made significant progress in both areas – we used the FRET sensors for glucose and sucrose to identify a new class of sugar transporters, the SWEETs. Key discoveries in 2014 include: (i) identification and characterization of SWEETs as hexose and sucrose transporters in model species and crops; (ii) identification of SWEETs as key players in phloem loading, seed filling, nectar secretion and pathogen susceptibility; (iii) identification of a subset of SWEETs involved in vacuolar transport of hexoses; (iv) identification of bacterial and human SWEET homologs; (v) atomic structure of two bacterial SWEET homologs; and (vi) identification of oligomeric states of SWEETs as potential means of regulating activity. This series of discoveries lays the basis for more rational approaches towards rational engineering of carbon allocation in plants and beyond.

Mechanism and Function of the Chaperonin from *Methanococcus maripaludis*: Implications for Archaeal Protein Homeostasis and Energy Production

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Funding: \$170,000 (2014)

PROGRAM SCOPE

Archaea offer a potentially cost effective and renewable source of energy. This proposal is focused on understanding the cellular substrates and mechanism of action of the group II chaperonin complex Mm-Cpn, the central chaperone of the methanogen *M. maripaludis*, which obtains energy by sequestering H₂ and reducing CO₂ to methane by the methanogenic pathway. More recently, it has also been suggested that the methanogenesis pathway could be run in reverse, to produce H₂ growing the organism in formate. We envision these efforts as a first step in obtaining a multi-level understanding of archaeal protein homeostasis, which will be instrumental for improving the functionality and design of the

enzyme pathways and complexes involved in energy production and storage. One additional importance consequence of a better understanding of archaeal protein homeostasis will be to increase their stress resistance, since their utilization for the efficient large-scale production of methane (and eventually also of H₂) requires that the organisms are resistance to a range of growth conditions.

FY 2014 HIGHLIGHTS

1) Establish pipeline for proteomic analyses of chaperone interactions in *M. maripaludis*. The homo-oligomeric ring shaped Mm-Cpn is the central chaperone in *M. maripaludis*. Because several enzymes in the methanogenesis pathway were substrates of the chaperonin, we decided to examine the substrate flux through the chaperonin. To this end, we established a system to grow *M. maripaludis* in the lab under conditions where we can carry out stable isotope labeling by amino acids in cell culture (SILAC) using ¹⁴N or ¹⁵N containing media that provided either H₂ or formate as electron donors for methanogenesis. Because the commercially available mass spectra deconvolution programs lack information for this organism, we are collaborating with the lab of Al Burlingame (UCSF) who has developed an in-house algorithm for the deconvolution of SILAC data.

2) Develop a new approach for identifying covariation. Statistical coupling analysis (SCA) can identify clusters of co-evolving residues within a protein family which form spatially contiguous functional networks. Coupling analyses have heretofore largely been restricted to small domains and monomeric proteins and could not be applied to large proteins with conserved domain for which few (less than one thousand) sequences are available. We have devised and implemented a novel statistical coupling metric, named Mutual Information for Statistical Coevolution (MISC), which renders analysis of very conserved, sparsely sequenced protein families. MISC constitutes an agnostic information theoretical measure which quantifies the degree of coupling between two columns in a multiple sequence alignment. Formally, it consists of the well-known variation of information which has been normalized by the joint entropy. Importantly, MISC depends very little on conservation, which is a considerable failing of many other available coupling metrics.

Structure Biology of Membrane Bound Enzymes

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Funding: \$300,000 (2014-2015)

PROGRAM SCOPE

The overall goal of the proposed research is to understand the membrane-associated active processes catalyzed by an alkane ω -hydroxylase (AlkB) from eubacterium *Pseudomonas oleovorans*. AlkB performs oxygenation of unactivated hydrocarbons found in crude oils. The enzymatic reaction involves energy-demanding steps in the membrane with the uses of structurally unknown metal active sites featuring a diiron [FeFe] center. At present, a critical barrier to understanding the membrane-associated reaction mechanism is the lack of structural information. The structural biology efforts have been challenged by technical difficulties commonly encountered in crystallization and structural determination of membrane proteins. The specific aims of the current budget cycle are to crystallize AlkB and initiate X-ray analysis to set the stage for structural determination. The long-term goals of our

structural biology efforts are to provide an atomic description of AlkB structure, and to uncover the mechanisms of selective modification of hydrocarbons. The structural information will help elucidating how the unactivated C-H bonds of saturated hydrocarbons are oxidized to initiate biodegradation and biotransformation processes. The knowledge gained will be fundamental to biotechnological applications to biofuel transformation of non-edible oil feedstock. Renewable biodiesel is a promising energy carry that can be used to reduce fossil fuel dependency. The proposed research capitalizes on prior BES-supported efforts on over-expression and purification of AlkB to explore the inner workings of a bioenergy-relevant membrane-bound enzyme.

FY 2014 HIGHLIGHTS

In the first three months of BES support, we have initiated large-scale production of AlkB by heterologous expression in *E. coli* and defined conditions for AlkB solubilization, purification and stabilization.

Functional Genomics Analysis of Plant Resistance to Pathogens: Impact of the Cell Wall

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

Relatively little is known about the types of cell wall alterations that affect disease resistance. In this research, we will investigate the effects of cell wall changes on disease resistance using the reference plant *Arabidopsis thaliana*. Aim 1. Create multiply-mutant plant genotypes with more severe cell wall structure and disease phenotypes. By testing *Arabidopsis* mutants with altered cell walls for changes in disease susceptibility, we have already identified several changes that impact disease resistance, including changes in the amount and methylation state of pectins. Due to genetic redundancy, most mutations have modest effects on the cell wall and on disease resistance. We will combine mutations with modest effects to create genotypes with larger changes in cell wall structure and disease resistance. These multiply-mutant genotypes will provide greater power for determination of the mechanisms underlying the effects of cell wall changes on disease resistance. Aim 2. Determine the nature of perturbations in the plant defense system responsible for altered disease phenotypes in cell wall mutants. Some changes in cell wall composition affect disease resistance through alterations in the levels of plant hormones involved in regulation of defense responses. We will examine mutants with altered cell walls to determine whether canonical defense signaling responses are affected. As our earlier work implicates a role for changes in pectin methylesterification in plant defense, we will also monitor activity of pectin methylesterases during responses to pathogen attack.

FY 2014 HIGHLIGHTS

We have published a paper describing our studies showing that the activity of pectin methylesterases increases in response to pathogen attack, with concomitant decreases in pectin methylesterification in the cell wall. These changes are under control of the jasmonic acid sector of the plant immune signaling

system. Plants with mutations in multiple pectin methylesterase genes are more susceptible to pathogen attack. Gerit Bethke, G., Grundman, R.E., Sreekanta, S., Truman, W., Katagiri, F., and Glazebrook, J. *Arabidopsis* PECTIN METHYLESTERASES Contribute to Immunity Against *Pseudomonas syringae*. *Plant Physiology* 164:1093-1107. DOI: doi:10.1104/pp.113.227637 (2014). We have nearly completed a second study showing that *gae1 gae6* double mutant plants have dramatically reduced levels of pectin in the cell walls, resulting in a brittle leaf phenotype. These plants are also more susceptible to the pathogens *Botrytis cinerea* and *Pseudomonas syringae*. This susceptibility may be due to differences in generation of oligogalacturonides, signaling molecules produced from pectin, as the mutant plants respond differently to treatment with macerozyme, an enzyme that releases oligogalacturonides from pectin. The mutants are also hyper-responsive to activation of jasmonate signaling. It is likely that the reduction in pectin causes perturbation of multiple processes affecting plant immune responses. A manuscript describing this work will be submitted for publication in early 2015.

Using the Corngrass1 Gene to Enhance the Biofuel Properties of Crop Plants

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

The development of novel plant germplasm is vital to addressing our increasing bioenergy demands. The major hurdle to digesting plant biomass is the complex structure of the cell walls, the substrate of fermentation. Plant cell walls are inaccessible matrices of macromolecules that are polymerized with lignin, making fermentation difficult. Overcoming this hurdle is a major goal toward developing usable bioenergy crop plants. Our project seeks to enhance the biofuel properties of perennial grass species using the Corngrass1 (Cg1) gene and its targets. Dominant maize Cg1 mutants produce increased biomass by continuously initiating extra axillary meristems and leaves. We cloned Cg1 and showed that its phenotype is caused by over expression of a unique miR156 microRNA gene that negatively regulates SPL transcription factors. We transferred the Cg1 phenotype to other plants by expressing the gene behind constitutive promoters in four different species, including the monocots, Brachypodium and switchgrass, and dicots, *Arabidopsis* and poplar. All transformants displayed a similar range of phenotypes, including increased biomass from extended leaf production, and increased vegetative branching. Field grown switchgrass transformants showed that overall lignin content was reduced, the ratio of glucans to xylans was increased, and surprisingly, that starch levels were greatly increased. The goals of this project are to control the tissue and temporal expression of Cg1 by using different promoters to drive its expression, elucidate the function of the SPL targets of Cg1 by generating gain and loss of function alleles, and isolate downstream targets of select SPL genes using deep sequencing and chromatin immunoprecipitation. We believe it is possible to control biomass accumulation, cell wall properties, and sugar levels through manipulation of either the Cg1 gene and/or its SPL targets.

FY 2014 HIGHLIGHTS

The separation of male and female flowers in maize provides the potential for independent regulation of traits that affect crop productivity. For example, tassel branch number controls pollen abundance and

length of shedding time, while ear row number directly affects kernel yield. Mutations in duplicate SBP-box transcription factor genes, unbranched2 (*ub2*) and unbranched3 (*ub3*), affect both of these yield traits. Double mutants display a decrease in tassel branch number and an increase in ear row number, both of which are enhanced by loss of a related gene called tasselsheath4 (*tsh4*). Furthermore, triple mutants have more tillers and leaves, phenotypes seen in Corngrass1 mutants that result from widespread repression of SBP-box genes. Immunolocalization of UB2 and UB3 proteins revealed accumulation throughout the meristem, but absence from the central domain of the meristem where cells regenerate. Thus, *ub2*, *ub3* and *tsh4* function as redundant factors that limit the rate of cell differentiation to the lateral domains of meristems. When these genes are mutated, cells are allocated to lateral primordia at a higher rate, causing a net loss of cells from the central domain and premature termination of the inflorescence. The *ub3* locus is tightly linked to QTL for ear row number and tassel branch number in both the NAM and IBM populations of maize recombinant inbreds, indicating that this gene may be agronomically important. Analysis of ear and tassel QTL across biparental families suggests that multiple mutations in *ub3* independently regulate male and female inflorescence development.

Bioenergy Production by a Photosynthetic Bacterium

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Funding: \$170,000 (2014)

PROGRAM SCOPE

Photosynthetic organisms are ideal models for understanding the biological basis of solar energy capture and as platforms for biofuel production. The purple nonsulfur photosynthetic bacterium *Rhodospseudomonas palustris* generates ATP from light by cyclic photophosphorylation, and thus its energy-generating machinery is separate from the rest of its metabolism. It has the ability to take up energy-poor compounds from its environment, remove electrons from them and then energize the electrons with energy from light for use in catalyzing reduction reactions that are not ordinarily thermodynamically favorable. It can do this at low light intensities. These capabilities provide *R. palustris* the opportunity to produce reduced carbon compounds that may be useful as biofuels or as substitutes for common petroleum-derived chemicals. The objective of this proposal is to understand at the molecular level how *R. palustris* adjusts to low light intensities to maximize photophosphorylation by dense layers of cells. *R. palustris* encodes a complex signal transduction system that allows it to respond to low light to increase its photosynthetic efficiency. The molecular details of how this low light signal transduction system operates will be investigated.

FY 2014 HIGHLIGHTS

An analysis of 16 closely related strains of *R. palustris* revealed that most strains have five sets of light harvesting genes. These are designed LH2a, LH2b, LH2e, LH3 and LH4. Two of these gene sets, LH2a and LH4 are expressed at much higher levels under low light conditions. Under extremely low light conditions ($< 1\mu\text{E}/\text{m}^2/\text{s}$; equivalent to the amount of light coming in through the crack at the bottom of a closed closet door), the LH4 genes are required for optimal growth. However, expression of other LH complexes compensates to a certain extent for the lack of LH4. We carried out experiments that lead to

a model for regulation of LH4 gene (*pucBA*) expression via a series of signaling proteins that respond to light and redox signals. We studied in detail two bacteriophytochromes (Bph2/Bph3) that are an essential component of the LH4 signal transduction cascade. These proteins sense light quality to fine-tune LH4 expression and are part of a phosphorelay leading to LH4 gene expression. We identified a protein (Rp3018) is responsible for sensing light intensity and we have evidence that it does so by sensing light intensity as a redox signal. We determined that it has two redox sensitive cysteines.

Structure, Function and Reactivity of CO Dehydrogenase from *Oligotropha carboxidovorans*

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Funding: \$168,320 (2014)

PROGRAM SCOPE

All biological metabolic pathways involve the storage and utilization of energy in the form of chemical bonds, and the biological interconversion of energy-relevant one-carbon compounds such as CO and CO₂ is directly relevant to the mission of the Department of Energy. The project focuses on the reaction mechanism of the enzyme CO dehydrogenase from *Oligotropha carboxidovorans*, which catalyzes the oxidation of CO to CO₂ and whose active site consists of a unique binuclear center comprised of μ -sulfido-bridged Mo(VI) and Cu(I) ions. This enzyme catalyzes the key step in the organism's growth on CO as sole source of carbon and energy. The reaction is a critical one in the interconversion of one-carbon compounds, and the unique binuclear active site constitutes an extremely promising new avenue to pursue in the development of a new generation of inorganic catalysts.

FY 2014 HIGHLIGHTS

In the past funding cycle we have completed and published two studies, focusing on the initial CO adduct formed in the course of the reaction of enzyme with H₂. In the first, we have used ENDOR spectroscopy to establish that CO binds to the Cu(I) of the binuclear center prior to being oxidized by the Mo(VI), allowing us to develop a comprehensive reaction mechanism that will be tested in future studies. In the second, we have fully characterized the oxidation of H₂ by the enzyme and developed a reaction mechanism modeled on that for reaction with CO. We have also identified a new EPR signal arising from the Mo(V)•Cu(I) binuclear center in complex with carbonate and are exploring the catalytic relevance of this putative enzyme•product complex.

G Protein Regulation of Energy Perception, Conversion, and Storage

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Funding: \$379,949 (2014-2015)

PROGRAM SCOPE

It is well established that sugars modulate photosynthesis both directly and through transcriptional control. This proposal deals with energy (glucose) perception, conversion (photosynthesis efficiency), and storage (carbohydrate sink). A body of new evidence, much of it from the last funding cycle, indicates that photosynthesis is regulated, in part, via a signaling pathway coupled by the single heterotrimeric G protein complex in *Arabidopsis*. Within this G protein complex resides a 7-transmembrane protein, AtRGS1, which likely serves as a cell surface co-receptor for D-glucose. Biochemical and structural properties of this complex make it stand out as unusual. First, AtRGS1 contains at its cytoplasmic C terminus a Regulator of G Signaling (RGS) box which accelerates the intrinsic GTPase activity of the *Arabidopsis* α subunit (AtGPA1). Second, unlike all known α subunits, the guanine nucleotide (GTP/GDP) exchange rate for AtGPA1 is spontaneous. In the previous grant cycle, we solved the structural requisites for this unique property and created novel α subunits with controllable activation states. We showed that the rate-limiting step in cycling between the active AtGPA1 (GTP bound) and inactive AtGPA1 (GDP bound) resides at the GTP hydrolysis step, not the nucleotide exchange step and that this is controlled by D-glucose, AtRGS1, AGB1, and WNK1 and WNK8 (kinases). We hypothesize that AtGPA1 is in equilibrium between two complexes and that glucose shifts the equilibrium to permit free AGB1 to recruit WNK kinases that phosphorylate AtRGS1 leading to physical uncoupling of AtRGS1 from self-activating AtGPA1 in a dose/duration-dependent manner. We will reconstitute these molecules *in vitro* and test association partners, rate constants, and affinities over a range of glucose. We will determine the structural requisites for association and the glucose effect using NMR and 2-D x-ray crystallography.

FY 2014 HIGHLIGHTS

Critical to success is the *in vitro* production of full-length AtRGS1 protein. Purification of seven-transmembrane proteins is difficult. We tried every expression system including, *E. coli*, plant cells, yeast, insect cells and human cells without significant enrichment of AtRGS1. Therefore, we turned to a cutting-edge technique of *in vitro* translation of membrane proteins. While *in vitro* translation is not new, this technique until the last few years could not be applied to membrane proteins. With *in vitro* translation, we are now able to express full-length AtRGS1 protein to the levels we need for biochemical analyses. We are presently optimizing expression and purification. Nanodisc technology is a method to stabilize membrane proteins in lipid disks that are scaffolded by belt proteins. We are currently examining the quality of these nanodisc particles using 2-D crystallography.

EARLY CAREER: Utilization of Protein Film Electrochemistry to Characterize the Mechanisms Imparting Aerotolerance and Bidirectionality in Soluble, Multimeric [NiFe]-Hydrogenases

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Funding: \$150,000 (2014)

PROGRAM SCOPE

Enzymes catalyze a number of energetically relevant multielectron redox transformations at metallocenter active sites that feature only earth abundant, first row transition metals. Importantly, this catalysis is often fast and reversible. Hydrogenases are the biological catalysts for the two electron reduction of protons to hydrogen, and, as such, they have received widespread interest for energy-related applications and as models for multielectron biological redox catalysis. However, it is still unclear how the catalytic properties of these enzymes are controlled at the atomic level, and, in particular, how ensembles of redox active cofactors work together to control movement of multiple electrons simultaneously. The objective of this project is to characterize the mechanisms controlling (1) the direction of catalytic bias towards either hydrogen oxidation or proton reduction, (2) the rates of catalysis, and (3) the susceptibility towards oxidative inactivation of the class of hydrogenases known as soluble, group 3 [NiFe]-hydrogenases and to compare these properties to those of other hydrogenases. These goals are being achieved via electrochemical characterization of hydrogenases from diverse biological sources including especially the hyperthermophilic archaean *Pyrococcus furiosus*.

FY 2014 HIGHLIGHTS

In Fiscal Year 2014, the electrocatalytic activity of the soluble hydrogenase I from *Pyrococcus furiosus*, (PfSHI) has been characterized under a number of conditions in collaboration with Prof. Michael Adams (UGA). This showed:

- 1) The proton reduction activity is highly dependent on temperature such that the bias of the enzyme shifts to strongly favor proton reduction under physiological conditions. This shift arises primarily from an increase in proton reduction activity since H₂ oxidation activity is unchanged;
- 2) PfSHI retains nearly 100% of its proton reduction activity in the presence of 1% oxygen over the entire temperature range investigated;
- 3) aerobic, oxidative inactivation results in the formation of two states with distinct redox properties;
- 4) PfSHI retains some hydrogen oxidation activity in the presence of brief bursts of oxygen. This oxygen-tolerance is more pronounced at higher temperatures;
- 5) Hydrogen oxidation activity is also maintained during long (15 minute) exposures to oxygen, but the inactive state requires longer reduction to reactivate.

The *Rhizobial* Nitrogen Stress Response and Effective Symbiotic Nitrogen Fixation

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Funding: \$360,000 (2014-2015)

PROGRAM SCOPE

We are investigating unusual mutants of *Sinorhizobium meliloti*, a symbiotic partner of forage crops like alfalfa and sweet clover. These mutants fix dinitrogen at a normal rate (e.g. they are Fix+) but they are not effective in supporting improved plant growth on nitrogen-free media (e.g. they are Eff⁻). Others

have reported a few Fix⁺Eff⁻ mutants, but our mutants appear to have the tightest and most reproducible phenotype. Our strains have a mutation in the N-terminus of *glnD*, the major NSR sensor in the bacteria that inactivates a domain responsible for uridylylating the PII proteins in response to nitrogen stress. Unlike the situation in *E. coli*, GlnD in *S. meliloti* appears to be able to regulate aspects of cellular physiology independently of the PII proteins. The Fix⁺Eff⁻ phenotype contains a puzzle—how is it possible for the bacteroids to fix nitrogen at a normal rate without benefiting the plants? The problem is not in general nitrogen assimilation; we have shown that the fixed nitrogen leaves the nodules and that the nodulated plants can assimilate other nitrogen sources, like urea. We proposed that the bacteria were synthesizing some nitrogen-containing compound that the plant could not catabolize and export of this compound from the nodules would not relieve the plant's nitrogen stress. We have identified a candidate compound, pyruvate canaline oxime (PCO), which is abundant only in mutant nodules and are focusing on its metabolism. In addition to representing a totally unexpected metabolism in the nodules, understanding the behavior could have very useful implications. One hypothesis is that, if we can divert a limited amount of nitrogen to a compound like PCO in a way that alfalfa was not overcommitting to this synthesis, it would compensate for the sink by fixing more nitrogen to restore normal nitrogen levels, increasing the total nitrogen fixation by the plants.

FY 2014 HIGHLIGHTS

In late 2013, we purified a compound that was substantially enriched in the mutant nodules. A preliminary structure was assigned on the basis of ¹³C-¹H NMR spectroscopy of the plant compound. This was confirmed in 2014 by synthesizing PCO in two steps: first by treating commercially available canavanine, a non-protein amino acid analog of arginine common in alfalfa, with an arginase we cloned from *S. meliloti*. This generates canaline, an ornithine analog that has an aminoxy group at the end of the R moiety of the amino acid; and then by reacting canaline with pyruvate. This compound has a ¹³C-¹H NMR spectrum identical to the GlnD nodule metabolite, confirming our identification. In collaboration with an analytical laboratory at UC Davis, we have developed HPLC procedures for quantifying PCO and related metabolites, including canavanine, canaline, homoserine and other oximes and are using this information in trying to figure out what is occurring in the mutant nodules. We have also made a ¹³C version of PCO to aid in quantitation using mass spectrometry.

Ferredoxin-Dependent Plant Metabolic Pathways

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Funding: \$300,000 (2014-2015)

PROGRAM SCOPE

The iron-sulfur protein ferredoxin serves as the physiological donor for many enzymes that play key roles in carbon, nitrogen and sulfur metabolism in oxygen-evolving photosynthetic organisms. Ferredoxin, which is reduced by Photosystem I in a light-dependent process, also serves as the electron donor for the thioredoxin-dependent regulation of enzymes involved in many metabolic pathways and as the electron donor in a key step in the synthesis of phycobilins – pigments involved in both light-harvesting and in signaling cascades. The proposed research is designed to elucidate the mechanisms of

five enzymes that use ferredoxin as the electron donor and to discover the details of the interactions of ferredoxin with these different enzymes, all of which form protein/protein complexes with ferredoxin.

FY 2014 HIGHLIGHTS

A flash-photolysis study has provided the first data on the kinetics of electron transfer from photo-reduced ferredoxin to a cyanobacterial nitrate reductase. The data demonstrate that the first electron transferred to the enzyme resides on its Mo center and that transfer of a second electron to the enzyme's Fe-S cluster is required to complete the catalytic cycle. Site-directed mutagenesis and computer modeling have produced a model for the 1:1 complex between a cyanobacterial ferredoxin and glutamate synthase. Conclusive evidence was obtained showing that a conserved 27-amino acid loop unique to this family of enzymes is not part of the ferredoxin-binding domain. The enzyme APS reductase provides the substrate for ferredoxin-dependent sulfite reductase. We have demonstrated, using deletion and over-expression *Arabidopsis* lines that one of the chloroplast isoforms of this enzyme also plays a key role in glucose signaling and flowering timing.

Transmethylation Reaction during Methylophilic Methanogenesis in Methanogenic Archaea

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Funding: \$165,000 (2014)

PROGRAM SCOPE

Most methane produced from biological sources comes from methanogenic Archaea. Of these organisms, *Methanosarcina spp.* and their relatives have the most diversified substrate range. Our overall goal is to understand the enzymes and molecular biology underlying these methanogenic pathways. We have primarily focused on methanogenesis from monomethylamine (MMA), dimethylamine, and trimethylamine (TMA). Methanogenesis from these substrates is begun by three methyltransferases (respectively, MtmB, MtbB, and MttB) that methylate cognate corrinoid proteins (respectively, MtmC, MtbC, and MttC), which are then used to methylate coenzyme M, forming the direct precursor of methane. The methylamine methyltransferases are non-homologous, yet each of their encoding genes contains an in-frame UAG codon. Metabolism of methylamines obligately depends on translation of an amber codon as the 22nd amino acid, pyrrolysine (Pyl). In previous periods, we have made inroads into understanding how pyrrolysine is biosynthesized, and how it is genetically encoded. Our current focus is to examine the function of pyrrolysine in the methylamine methyltransferases. Our operating hypothesis has been that this amino acid acts to bind and orient methylamines for methyl transfer to the Co(I)-corrinoid protein. Our approaches include site directed mutagenesis of Pyl-containing methyltransferases, study of naturally occurring homologs lacking Pyl, and physical methods to detect pyrrolysine interaction with methylamines.

FY 2014 HIGHLIGHTS

We published a paper in PNAS in collaboration with D. Ferguson on DSY3156, a non-Pyl MttB homolog from *Desulfitobacterium hafniense*. We showed the enzyme is a glycine:corrinoid methyltransferase

operating at unit stoichiometry. DSY3157, an adjacently encoded protein to DSY3156, is a methylcobalamin:tetrahydrofolate methyltransferase, adding further support to our hypothesis DSY3156/3157 act to methylate THF for subsequent oxidation to catabolically reduce an external electron acceptor. DSY3156 cannot use TMA, unlike methanogen Pyl MttB enzymes. In still unpublished work, we predicted residues of the glycine betaine methyltransferase that would bind glycine betaine, and replacement of these residues was found to drastically reduce catalysis. Furthermore, we collaborated with Dr. Bing Hao who crystallized the protein in complex with glycine betaine. The preliminary structure confirmed our predicted binding site. An overlay of the structures of the pyl-MttB (in collaboration with Michael Chan) and the non-Pyl glycine betaine methyltransferase reveals that pyrrolysine occupies a position overlapping the glycine betaine binding residues of DSY3156. We have now obtained purified recombinant MttC and Pyl-containing MttB by expression of the *Methanosarcina barkeri* genes in *Methanosarcina acetivorans*. Additionally, we now have stable recombinant RamA, which activates the corrinoid protein. We have assayed MttB by direct MttC methylation and found an apparent turnover rate of 200 min⁻¹. We measured the preparations of two variant MttB lacking pyrrolysine, and found they possess an approximately 1000-fold lower activity relative to wild type MttB, consistent for a catalytic role for pyrrolysine. The residual rate in the mutants lacking pyrrolysine may be due to the presence of trace amounts of wild type MttB enzyme from the *M. acetivorans* host, but if we find it is due to the mutant enzyme, this may dictate re-evaluation of the current model for pyrrolysine function.

Unraveling the Regulation of Terpenoid Oil and Resin Biosynthesis for the Development of Biocrude Feedstocks

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Funding: \$170,000 (2014)

PROGRAM SCOPE

This project is aimed at developing single cell approaches to investigate plant cell types that are specialized for oil and resin biosynthesis. We are currently using three experimental model systems that accumulate valuable terpenoid feedstock chemicals: (1) peppermint glandular trichomes (l-menthol), (2) Citrus secretory cavities (d-limonene), and (3) loblolly pine resin ducts (α/β -pinene and abietic acid).

Peppermint: We have been very successful in modulating the endogenous essential oil pathway of peppermint to accumulate different intermediates, in particular l-limonene, (+)-pulegone and (+)-menthofuran.

Citrus: We have completed a comprehensive study of the ultrastructural changes associated with the development of secretory cavities in Citrus peel. We have been particularly interested in understanding the role of membrane contact sites between endoplasmic reticulum and leucoplasts, as these might be characteristic of epithelial cell types with high terpenoid secretory activity. We have also localized (+)-limonene synthase, the enzyme responsible for >90% of carbon flux into terpenoids in epithelial cells of secretory cavities, to specific areas of leucoplasts.

Pine: we have acquired cell type-specific transcriptome data for epithelial cells that surround resin ducts in loblolly pine needles. These data sets provide a first glimpse of the developmental and biosynthetic factors that play important roles in the initiation and filling of resin ducts.

Enzyme structure-function: We have acquired the first comprehensive data set to map the active site of a model monoterpene synthase ((-)-limonene synthase) and evaluated residues with a potential functions to stabilize carbocation reaction intermediates and to serve as catalytic base in the hallmark deprotonation reaction of this class of enzymes.

FY 2014 HIGHLIGHTS

Terpene synthases catalyze chain length-specific, electrophilic cyclization reactions that constitute the first committed step in the biosynthesis of structurally diverse terpenoids. During the current funding period, we used crystal structural data for (4S)-LS of spearmint (*Mentha spicata* L.) to infer which amino acid residues are positioned in close proximity to the substrate and carbocation intermediates of the enzymatic reaction. Mutation of residues W324 and H579 caused a significant drop in enzyme activity and formation of products (myrcene, linalool and terpineol) characteristic of a premature termination of the reaction. A double mutant (W324A/H579A) had no detectable enzyme activity, indicating that either binding of the substrate or the terminal deprotonation reaction was impaired. Exchanges to other aromatic residues resulted in enzyme catalysts with significantly reduced activity. These results are consistent with a critical role of W324 and H579 in the stabilization of carbocation intermediates. The ultimate step of the (4S)-LS reaction cascade is the deprotonation from a carbocation and release of the olefin final product. H579 has the properties of a catalytic base and, in one energy-minimized docking orientation of the α -terpinyl cation, is positioned close to the proton to be removed. W324 is situated close to the leaving proton in an alternative docking orientation of the α -terpinyl cation. The significant reduction of specific enzyme activity in all W324 mutants could be interpreted as evidence that the termination reaction (rather than the initial isomerization) has become rate-limiting. The fact that the W324/H579 double mutant had no measurable enzyme activity is consistent with a function of these residues as catalytic bases. A manuscript reporting these findings is currently in press at PNAS.

Electron Flow and Energy Conservation in a Hydrogenotrophic Methanogen

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

Our goal is to understand electron flow and energy conservation in hydrogenotrophic methanogens. Until recently it was not understood how methanogenesis from hydrogen and carbon dioxide led to the conservation of net energy sufficient for ATP production. The suggestion that electron bifurcation took place at the heterodisulfide reductase step appeared to solve the problem. Part of our effort is to show that electron bifurcation indeed takes place in hydrogenotrophic methanogens, and to learn about the electron flow pathways through the electron bifurcating protein complex. We also tested a corollary to the electron bifurcation hypothesis, that an energy-converting hydrogenase called Eha plays an anaplerotic role. We are determining the nature of the requirement for Eha and identifying the genes that are essential for its function. We are also working to determine the basis for apparent differences in efficiencies of energy conservation that occur under hydrogen-excess and hydrogen-limited conditions, manifested in changes in growth yields. Another aim is to learn more about the role of formate as an

alternative electron donor to hydrogen. Finally, we are studying the maturation of the iron hydrogenase Hmd by determining the phenotypes of mutants containing deletions of genes hypothesized to participate in Hmd cofactor synthesis.

FY 2014 HIGHLIGHTS

Recent work has focused on the proteins that deliver electrons to the electron bifurcating complex of hydrogenotrophic methanogens, represented by *Methanococcus maripaludis*. Flavin-based electron bifurcation has recently been characterized as an essential energy conservation mechanism that is utilized by hydrogenotrophic methanogenic Archaea to generate low-potential electrons in an ATP-independent manner. Electron bifurcation likely takes place at the flavin associated with the alpha subunit of heterodisulfide reductase (HdrA). In *Methanococcus maripaludis* the electrons for this reaction come from either formate or hydrogen via formate dehydrogenase (Fdh) or Hdr-associated hydrogenase (Vhu). However, how these enzymes bind to HdrA to deliver electrons was unknown. We found that the delta subunit of hydrogenase (VhuD) is central to the interaction of both enzymes with HdrA. When *M. maripaludis* was grown under conditions where both Fdh and Vhu were expressed, these enzymes competed for binding to VhuD, which in turn bound to HdrA. Under these conditions, both enzymes were fully functional and were bound to VhuD in substoichiometric quantities. We also showed that Fdh copurifies specifically with VhuD in the absence of other hydrogenase subunits. Surprisingly, in the absence of Vhu, growth on hydrogen still occurred; we showed that this involves another hydrogenase, F420-reducing hydrogenase. The data presented represent an initial characterization of specific protein interactions centered on Hdr in a hydrogenotrophic methanogen that utilizes multiple electron donors for growth.

Lignin Biopolymer Assembly and Primary Structure: A (Bio)Chemical Characterization

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Funding: \$180,000 (2014)

PROGRAM SCOPE

Nature's most abundant terrestrial carbon forms (plant biomass) are studied globally to maximize potential for renewable energy, optimal photosynthetic capture, and as sustainable sources of intermediate/fine chemicals and bioproducts/biofuels. This renewable carbon is largely lignified plant cell walls, and associated metabolites. A major bottleneck is in understanding cell wall polymeric lignins, Nature's second most abundant biopolymers next to cellulose. We thus still have very much to learn about plant cell wall formation and how their biomechanical properties are influenced by various lignins in different cell types/subcellular wall layers, as well as physiological roles of other biochemically related metabolites in these tissues. Our 3 interlocking objectives are to further: (i) develop cell specific metabolomic, proteomic, and transcriptomic approaches for holistic determination of distinct cell wall forming processes involved in lignin biosynthesis and related metabolism in wild type (WT) and mutant/genetically modified plant lines. We have developed methodology for much enhanced *in planta* metabolomics imaging, as well as targeted and untargeted metabolomics analyses of WT/transgenic *Arabidopsis* and poplar lines. In addition, transcriptome and proteomic analyses of these WT and

differentially lignin reduced lines have given new insights into metabolic cross-talk not previously contemplated; (ii) determine lignin primary structures/assembly mechanisms via comparison of cell-wall specific, WT and genetically modified lignins. Here, we have developed mass spectrometric fragmentation processes allowing determination of, as a model system, polystyrene primary structure and its fragmentation, with this approach now being applied to lignin primary structure and (iii) correlating lignin primary structures with biomechanical properties in distinct vascular plant cell wall types. The latter is being done with non-destructive biophysical testing methods.

FY 2014 HIGHLIGHTS

1. First 3D structure of a dirigent protein at 1.95 Å resolution and proposed implications for lignification (Kim *et al.*, J. Biol. Chem., in press).
2. MALDI imaging mass spectrometry *in situ* to enable detection, identification, localization and quantification of various metabolic classes (Marques *et al.*, Molecular BioSystems, 2014, 10:2838).
3. Putative proton relay mechanism assessment in *Arabidopsis* cinnamyl alcohol dehydrogenase catalysis AtCAD5 (Lee *et al.*, 2013, Organic Biomolecular Chemistry, 11:1127).

Chemo/Mechanical Energy Conversion via Supramolecular Self-Assembly

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Funding: \$380,000 (2014-2015)

PROGRAM SCOPE

The overall goal of this fruitful collaboration between Emory University and the Argonne/Oak Ridge/Brookhaven National Laboratories has been to development methods for directing the assembly of synthetic oligopeptide structures into nano-scale objects with a degree of order approaching that observed in biological systems. We have now designed and engineered a synthetic chemical gradient along the contour length of a series of peptide-based supramolecular assemblies. Two distinct, complementary self-assembling peptide nanostructures based on cross- β -based and α -helix-based nanotubes have made those accomplishments possible. We have already demonstrated organizing antenna complexes on a peptide bilayer surface for light harvesting and energy transfer, and are now positioned to engineer and define nanoscale actuators that mirror the complex biochemical cycle of physical and chemical energy inter-conversion via a completely new supramolecular form. These achievements are fundamental to creating a simple bio-inspired self-healing supramolecular assembly capable of emulating critical components of natural chemo/mechanical energy inter-conversion.

FY 2014 HIGHLIGHTS

Publications:

- Chen Liang, Rong Ni, Jillian E. Smith, W. Seth Childers, Anil K. Mehta, David G. Lynn, (2014). Kinetic Intermediates in Amyloid Assembly. J. Am. Chem. Soc 136: 15146–15149: doi: 10.1021/ja508621bP
- Sha Li; Anton N. Sidorov; Anil K. Mehta; Anthony J. Bisignano; Dibyendu Das; W. Seth Childers; Erin Schuler; Zhigang Jiang; Thomas M. Orlando; Keith Berland; David G. Lynn, (2014). Neurofibrillar

Tangle Surrogates: Histone H1 Binding to Patterned Phosphotyrosine Peptide Nanotubes. *Biochemistry* 53: 4225-4227.

- Neil R. Anthony, Anil K. Mehta, David G. Lynn and Keith M. Berland (2014) Mapping amyloid- β (16-22) nucleation pathways using fluorescence lifetime imaging microscopy, *Soft Matter*,10: 4162-4172.
- Qiaohang Guo, Anil K. Mehta, Martha A Grover, Wenzhe Chen, David G. Lynn and Zi Chen. Shape Selection and Multi-stability in Helical Ribbons, *Applied Physics Letters*,104(21):211102
- Jiang T, Xu C, Zuo X, Conticello VP. 2014 Structurally Homogeneous Nanosheets from Self-Assembly of a Collagen-Mimetic Peptide. *Angew Chem, Int Ed.* 53, 8367-71 doi: 10.1002/anie.201403780
- Jiang T, Xu C, Liu Y, Liu Z, Wall JS, Zuo X, Lian T, Salaita K, Ni C, Pochan D, Conticello VP. 2014 Structurally Defined Nanoscale Sheets from Self-Assembly of Collagen-Mimetic Peptides. *J Am Chem Soc.* 136, 4300-8 doi: 10.1021/ja412867z
- Xu C, Liu R, Mehta AK, Guerrero-Ferreira RC, Wright ER, Dunin-Horkawicz S, Morris K, Serpell LC, Zuo X, Wall JS, Conticello VP. 2013 Rational Design of Helical Nanotubes from Self-Assembly of Coiled-Coil Lock Washers. *J Am Chem Soc.* 135, 15565-78 doi: 10.1021/ja4074529

Multifunctional Ubiquitin-fold Proteins of Archaea

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Funding: \$300,000 (2014-2015)

PROGRAM SCOPE

The overall goals of this research project are to expand the scientific knowledge of archaeal cell physiology (with emphasis on an archaeal ubiquitin-like proteasome system) and use this insight to develop next-generation biocatalysts for the production of renewable fuels and chemicals. Ubiquitin is a small protein that is universal to eukaryotic cells and is isopeptide-linked to target proteins by an E1-E2-E3-mechanism named ubiquitylation. Ubiquitylation alters the stability and cellular localization of proteins and controls important processes of interest in metabolic engineering including cell division and metabolism. Recently, we found small archaeal modifier proteins (SAMPs) to be related to ubiquitin in 3-D structure, activated by an E1-like mechanism, and isopeptide linked to protein targets. SAMPs are also used for sulfur mobilization to form molybdopterin and 2-thiolated tRNA needed for anaerobic growth and translation fidelity at high temperature. The specific aims of this project are: 1) to determine the molecular factors that regulate the switch between sulfur mobilization and protein modification for the dual function SAMPs and 2) to ascertain whether SAMPs target proteins for degradation by proteasomes and can be used to alter protein stability. Our project supports DOE missions in alternative energy, global carbon cycling, and biogeochemistry and provides fundamental insights regarding the mechanisms non-medical microbes use to transduce and/or store energy. In particular, we expand the scientific knowledge of post-translational mechanisms that are linked to energy-dependent proteolysis by proteasomes which are essential in two domains of life (Eukarya and Archaea). In addition, we advance understanding of how ubiquitin-like proteins mediate sulfur relay (particularly during growth in conditions of anoxia and high temperature) and provide insight for their use in metabolic engineering.

FY 2014 HIGHLIGHTS

We hypothesize that non-covalent protein partners are important determinants in regulating the switch between sulfur mobilization and protein modification for the archaeal ubiquitin-proteasome system (UPS). Thus, initial investigations relied upon pull-down experiments to identify protein partners using SAMP1 as bait. SAMP1 was purified from recombinant *Escherichia coli*, immobilized on beads by amide linkage, and incubated in the presence of ATP with cleared cell lysate of *Haloferax volcanii* (the model archaeon of this study). Analysis of the proteins retained by the SAMP1-decorated beads revealed a prominent protein band of 250 kDa that was detected by SYPRO Ruby staining of non-reducing SDS-PAGE gels. Subsequent analysis by LC-MS/MS of tryptic peptides derived from this band identified proteins that were unique to the samples including Cdc48-type AAA ATPase, RNase J1 and RecJ-domain protein homologs. These findings were experimentally reproducible. Similar methods identified protein factors that associated with the E1-like UbaA including SAMP1-3 and rhodanese domain (RHD) proteins. To further understand these findings, genes encoding the RHD proteins were deleted, and the mutant strains were found deficient in sulfur relay but not ubiquitin-like protein modification. Our work also provides evidence for an ancient pathway of protein degradation in Archaea that is related to the N-end rule of eukaryotes. N-degrons were found to stimulate ubiquitin-like modification and subsequent degradation of certain proteins by proteasomes. Mutant strains deficient in various components of the archaeal UPS were found to stabilize specific N-degrons. In particular, phosphorylation of N-terminal penultimate serine residues, methionine aminopeptidase cleavage, protein acetylation, and fusion to N-StreptII tags were all found to alter protein stability by mechanisms that require archaeal UPS function.

Energetics and Kinetics of Syntrophic Aromatic Degradation

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

Syntrophic metabolism plays an essential role in the recycling of organic matter to methane and carbon dioxide in many environments. Syntrophy is a thermodynamically necessary interaction between a hydrogen- and formate-producing microbe and its hydrogen- and formate-using partner. A distinctive feature of syntrophic metabolism is the need for reverse electron transfer. The production of hydrogen or formate from electrons generated in the oxidation of acyl-CoA intermediates to their respective enoyl-CoA intermediates represents a considerable energy barrier. The membrane components involved in the generation and use of ion gradients are, thus, critical components of syntrophic metabolism. The objectives of this proposal are to: (1) detect the membrane complexes involved in reverse electron transfer, (2) conduct gene expression and operon analyses to determine if key gene systems are induced under growth conditions that require reverse electron transfer, thus, implicating these genes in this important biological function, (3), determine the function of a butyrate-induced, membrane complex in *Syntrophomonas wolfei* and (4) determine if *S. wolfei* and *S. aciditrophicus* have electron-bifurcating hydrogenases and formate dehydrogenases that could be used for reverse electron transfer of electrons from NADH to hydrogen or formate. We will use a combination of proteomic, gene expression, and biochemical approaches to test the role of the above systems and to detect novel complexes involved in

reverse electron transfer in syntrophic fatty and alicyclic acid metabolism. This bioenergetic study of syntrophy integrates genomic, functional genomic, and biochemical approaches to understand an essential and poorly characterized process critical for carbon cycling on the planet and will demonstrate how bacteria operate at free energy changes close to equilibrium.

FY 2014 HIGHLIGHTS

We found that *Syntrophus aciditrophicus* uses a novel mechanism for ATP from acetyl-CoA. This specialized bacterium uses pyrophosphate, an important prebiotic energy source, and the AMP-forming, acetyl-CoA synthetase (Acs1) to produce ATP. *S. aciditrophicus* uses AMP-forming, acyl-CoA synthetases to activate benzoate, cyclohexane-1-carboxylate, and crotonate to their respective coenzyme A (CoA) derivatives. The pyrophosphate formed during substrate activation can then be used by Acs1 to produce ATP, indicating the importance of pyrophosphate cycling in *S. aciditrophicus*. We used a combination of genomic, transcriptional and enzymatic analyses to determine the mechanism of interspecies electron transfer by two model syntrophic microorganisms, *Syntrophomonas wolfei* and *S. aciditrophicus*. Butyrate metabolism and methane production by washed cell suspensions of *S. wolfei* and *Methanospirillum hungatei* were inhibited by hydrogenase inhibitors (cyanide and carbon monoxide), but not by a formate dehydrogenase inhibitor (hypophosphite). Syntrophic benzoate oxidation and methane production by washed cell suspensions of *S. aciditrophicus* and *M. hungatei* were inhibited by hypophosphite, but not cyanide and carbon monoxide. All three inhibitors halted syntrophic cyclohexane-1-carboxylate metabolism. Thus, these syntrophic microorganisms have flexible metabolisms that allow them to use either hydrogen or formate transfer depending on the substrate involved. We delineated the major conduit for electron flow from butyryl-coenzyme A to hydrogen and formate in *S. wolfei*, which involves a membrane-bound, iron-sulfur oxidoreductase and a hydrogenase (Hyd2). In *S. aciditrophicus*, we showed that Rnf catalyzes the energetically unfavorable reduction of ferredoxin with NADH. Quantitative real time-polymerase chain reaction and proteomic studies provided strong evidence for the involvement of these enzyme systems in syntrophic metabolism.

Energy Conservation During Methanogenesis in *Methanosarcina* Species

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

The long-term goal of the proposed research is to expand our knowledge regarding energy-conservation during methanogenesis in *Methanosarcina* species. A central aspect of this study entails examination of the genotypic and phenotypic differences between *Methanosarcina barkeri*, an organism that grows well on H₂/CO₂, and *Methanosarcina acetivorans*, a closely related organism that is incapable of growth on H₂/CO₂. Our recent data show that hydrogen is a central intermediate in methanogenesis from all known substrates in *M. barkeri*, whereas *M. acetivorans* has evolved to specifically exclude hydrogen as an intermediate. The differences in hydrogen metabolism lie at the center of the energy-conserving electron transport chains of the two organisms. By examining the molecular, genetic, biochemical and physiological traits that underpin these differences we expect to deepen our overall understanding of

methanogenesis, hydrogen production/consumption and energy conservation during anaerobic metabolism; all of which are central themes in the BES Physical Biosciences research program. Three specific issues regarding the mechanisms of energy conservation in *Methanosarcina* are addressed in the proposed experiments. First, we will characterize the molecular mechanism of energy conservation via hydrogen-cycling in *M. barkeri*. Second, we will characterize the hydrogen-independent, energy-conserving electron transport chain in *M. barkeri*. Third, we will characterize the hydrogen-independent, energy-conserving electron transport chain in *M. acetivorans*. The proposed experiments will utilize recently developed methods for genetic analysis of *Methanosarcina*; however, physiological, biochemical and molecular approaches will complement the genetic approach. This strategy is expected to generate data that are both novel and complementary to the results of preceding studies.

FY 2014 HIGHLIGHTS

In the past year, our work has focused on characterizing mechanism by which hydrogen is efficiently recaptured during hydrogen-cycling electron transport. Two possible mechanisms were tested. In the first, the activity of the periplasmic hydrogenase would be much higher than that of the cytoplasmic hydrogenase. To examine this idea, we conducted a thorough analysis of hydrogenase activity in a panel of mutants that lack the periplasmic Ech and Vht hydrogenases, as well as the cytoplasmic Frh hydrogenase, in all possible combinations. These data show that the H₂ production/consumption of Vht and Frh are roughly balanced, with somewhat higher levels of Vht activity. Thus, while it remains a possibility, it is not obvious whether the excess uptake of H₂ by Vht suffices to explain the phenotype. In the second mechanism, H₂ produced by cytoplasmic Frh would be channeled to the periplasmic Vht in a way that would prevent diffusive loss. We hypothesized that such channeling would require close association of the cytoplasmic and periplasmic hydrogenases, perhaps involving a membrane protein channel to facilitate efficient hydrogen transfer. To examine this, we employed high-resolution fluorescence microscopy to visualize the localization of Frh. We showed that the SNAP system worked in *M. barkeri* and that Frh appears to be localized to the inner face of the cytoplasmic membrane in support of a channeling mechanism. Global transcriptional profiling (RNA-seq analysis) of the hydrogenase mutants showed that transcription of the hydrogenase genes was not significantly altered, but the *fpo* operon was strongly induced whenever *frh* was deleted. Thus, because the branched electron transport chain diverges at Frh/Fpo, it appears that electron flux between the H₂-cycling and H₂-independent electron transport chain is at least partially controlled at the transcriptional level in a manner that requires Frh.

Regulation of Plant Cells, Cell Walls, and Development by Mechanical Signals

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Funding: \$230,000 (2014)

PROGRAM SCOPE

The goal of the project is to test and extend a new view of plant development, in which mechanical signals between cells in growing tissues play a role as critical as that of chemical signals. Earlier work has shown that the microtubule cytoskeleton of the epidermal cells of the meristem aligns parallel to the

principal direction of maximal stress when stress is anisotropic, and that the PIN1 auxin transporter, responsible for auxin movement between shoot meristem cells in the inflorescence stage is mechanically controlled, such that it accumulates preferentially in the most stressed side wall of each epidermal cell. As auxin makes cells expand, and this expansion creates stress on neighboring cells, there is a general tendency for auxin to move from cells with lower auxin to those with higher. This has been shown by computational models to generate known phyllotactic patterns. Computational models of growing meristems that include these mechanical feedbacks show behavior very much like that of the meristems themselves. There are nonetheless many unanswered questions. The specific research goals of the current period of funding have been to answer several of these: first, can we show that the predicted mechanical effects are due to physical forces and not other forms of cell-cell communication? Second, can we extend the model to new aspects of meristem growth, such as cell wall biosynthesis and cell division? Third, does mechanical signaling control growth in parts of the plant other than the meristem? And fourth, can we use the predicted feedbacks and computational models to further probe the mechanics and behavior of plant cells and plant cell walls? Answers to these questions will provide a more detailed understanding of the structure and dynamics of complex biological nanomaterials such as plant cell walls and cytoskeletal elements involved in energy capture, transduction, and storage.

FY 2014 HIGHLIGHTS

We have created a set of reversible treatments that change the stress patterns in a shoot apex, such as changing turgor with mannitol solutions, flattening with a coverslip, and local treatment with cell wall loosening enzymes (for example cellulases), and they all cause the predicted changes in PIN1 localization. Thus, the effects seen earlier were due to mechanics, and not wounding. We performed extensive sets of experiments with pavement cells of developing cotyledons, and found that the stress pattern in these cells with complex shapes (as predicted by finite element method models of the cells and of the tissue) correspond with their microtubule arrays, and with cell wall reinforcements detected by atomic force microscopy that are consistent with the expected properties of cellulose fibrils. As stresses in these cells are determined largely by cell shape, and vary in different cellular regions, we can add a third source of stress (tissue shape, local tissue expansion, and now cell shape) that feeds back to plant cells, and can infer that the mechanism by which the microtubules align to anisotropic stress are subcellular. Further experiments showed that stress changes induce microtubule severing, and that microtubule realignment to stress in the pavement cells requires the severing enzyme katanin. One additional prediction of the stress model is that auxin flow patterns in the meristem will depend on the properties of the cell wall, as its viscoelasticity is regulated by stress (via microtubules and cellulose synthesis). Any mutation that changes the viscoelasticity or ability to grow of the cell wall could therefore change phyllotactic pattern, as could mutations that affect PIN1 localization. We thus have a new way of probing for cell wall mutants.

Conformational and Chemical Dynamics of Single Proteins in Solution by Suppression of Brownian Motion

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Funding:	\$658,334 (2014-2016)

PROGRAM SCOPE

The primary objective of this project is to study and understand the behavior of individual photosynthetic proteins in a physiologically relevant solution environment. Single-molecule measurements have been firmly established as a cutting-edge technique for elucidating mechanistic details of numerous biological processes. These measurements are most powerful when they are applied over a long enough time to watch a process undergo multiple, statistically meaningful state transitions. Unfortunately, the immobilization of single biomolecules on surfaces that usually enables this long time window is often undesirably perturbative. To address this issue, we have constructed a microfluidic device, the Anti-Brownian ELectrokinetic (ABEL) trap, which uses microscopy and real-time feedback forces to cancel Brownian motion and trap a molecule in solution. Previously, we enhanced the performance of the trap to simultaneously measure fluorescence intensity, lifetime and spectrum for single fluorescent dyes. Because of these capabilities, the ABEL trap is particularly powerful in the study of the photodynamics of single photosynthetic pigment-protein complexes. For example, we discovered state-to-state transitions in the bacterial light-harvesting complex 2 (LH2) from purple bacteria which show that LH2 undergoes a photoactivated, reversible switch to a quenched conformation, providing a previously unknown photoprotective functionality. We are now addressing the critically important light-harvesting complex II (LHCII), the primary antenna from green plants, and other pigment-protein complexes. We are also developing and utilizing a dramatic new capability of the ABEL trap: the direct measurement of the transport properties of the trapped biomolecule in real-time, thus giving us access to the molecular size and charge. This capability is being used to sense protein-protein interactions, aggregation, and oligomerization.

FY 2014 HIGHLIGHTS

This project has yielded two significant accomplishments in the current fiscal year. In the first area, the ability of the ABEL trap to sense size and charge has been used to perform several unprecedented measurements of (a) the time-dependent hybridization and melting of an individual DNA molecule under equilibrium conditions, and (b) the dissociation and oligomerization state of single allophycocyanin (APC) pigment-protein complexes. The work paves the way toward multiple future studies of multi-component protein assemblies where it will be possible to directly measure the distribution and size of oligomers of biomolecules in a complex mixture. In the course of these explorations, the photoinduced pigment decay process in monomeric APC was fully determined. The second area addresses the known fact that higher plants and algae quench excess energy under high light, but the photophysical mechanisms behind this process are controversial. ABEL trap measurements of single LHCII complexes found an unusual array of transitions between states of different emission brightness and excited state lifetimes, which differ in several respects from more conventional measurements on surface-attached molecules. Extensive data acquisition and analysis led to the identification of three functional states, where one is an unquenched state and two are quenched states. The characterization of these newly-discovered states and measurements of the dynamics between them were performed. Simulation of conditions that mimic high light were achieved with pH changes and mutations of the pigment compositions. These experiments showed that, under the simulated high light conditions, the relative population of one of the quenched conformations increases, pointing to a possible molecular basis for quenching. To stimulate understanding, a theoretical model was developed to describe the microscopic mechanism behind the quenched states.

The Structure of Pectins

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PROGRAM SCOPE

Pectin is the most abundant polysaccharide in primary plant cell walls of dicots and has a very complex structure. The function of pectin in cell walls is not well understood, but modifications of the structure occur naturally during plant development and some mutations leading to modifications in structure have severe phenotypes. Pectin is composed of four structurally distinct regions each of which has its own complexity and may or may not be linked to each other. About half of the xyloglucan in cell walls is covalently linked to pectin and there is fairly strong evidence that the cell wall protein extensin is also covalently linked to pectin. It is our expectation that the primary plant cell wall is a covalently crosslinked network of polysaccharides (and sometimes protein) analogous to the bacterial peptidoglycan network and the glucan-mannoprotein-chitin network in yeast. One goal of the project is to characterize the linkages between the various regions of pectin and between pectin and the other polymers. To find the crosslinkages we will use cloned (monospecific) enzymes to degrade the polymers and separate out fragments which retain characteristics of two different polymers. These will then be characterized by NMR and mass spectroscopy. We have isolated and characterized oligosaccharides representing the crosslinkages between homogalacturonan and rhamnogalacturonan (RG) and between galactans and arabinans and RG during the previous grant period. It remains to be determined how xylogalacturonan and rhamnogalacturonan are linked together. We have also found that xyloglucan and RG are crosslinked via a highly branched 1-5 linked arabinan. We plan to characterize the connections between the arabinan and the xyloglucan and between the arabinan and the RG using the same fragmentation, separation, and characterization approach mentioned above.

FY 2014 HIGHLIGHTS

Xiaoyu Qiao, the graduate student, repeated our experiments on showing the linkage between xyloglucan and pectin in *Arabidopsis* suspension culture cell walls. This will allow us to finalize a manuscript describing the linkage. Xiangmei Wu, the post doc, characterized fragments of pectin produced by a combination of HF solvolysis and pectate lyase digestion. Some of the pieces make the argument that homogalacturonan is linked linearly to rhamnogalacturonan water tight. She also helped me characterize the less abundant fragments of Karaya gum that I made by HF solvolysis. (We had characterized the major fragments the previous year). We now have fragments representing the whole backbone of the polymer. Only the placement of the neutral sugar sidechains remains to be determined. We will use the fragments of Karaya gum as standards so that we can recognize them in normal pectins. Karaya gum is a plant exudate, used in the food industry, which resembles rhamnogalacturonan, but has some interesting features such as frequent GlcA substituents on the GalA and sometimes two GalA residues between Rha residues.

Functional Analysis and Genetic Manipulation of Plant ABCB Organic Ion Transporters

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PROGRAM SCOPE

In yeasts and plants, a large and diverse family of ATP-binding cassette (ABC) transporters mediates the movement of metabolites, cell wall monomers, secondary compounds involved in plant protection and signaling, lipids, xenobiotics, waxes, and metals. Implication of ABC transporters in monolignol and lipid export and secondary compound import make this class of transporters a primary target for efforts to enhance the quality of biomass destined for production of “drop in” biofuels and manufacturing precursors. At a mechanistic level, work from our lab has associated exclusion of hydrophobic compounds from the outer leaflet of cellular membranes with discrete sites in the B-subclass of ABC transporters and has associated substrate-specific binding and transport with protein sites associated with the inner leaflet of membranes. Reversible transport mediated by another group of ABCB transporters has been associated with unique regulatory sites in this subgroup of transporters. The goal of this project is to elucidate the structural basis of these interactions, to demonstrate that manipulation of these sites can be used to direct activity and specificity of the transporters and to ultimately custom design transporters that can move important energy-related precursors to improve accumulation and recoverability in plants, yeasts, and bacteria.

FY 2014 HIGHLIGHTS

Rapid turnover of plasma membrane ABC transporters is a limiting factor in efforts to express engineered, substrate-specific transporters. The ABCB4 substrate-activated transporter becomes unstable under multiple stress conditions and was used as a model to understand innate and transcriptional regulation of ABC transporter stability. The transcript level of ABCB4 was found to be negatively regulated by treatments with abscisic acid (ABA) or cytokinin (CK). Moreover, loss of function of an ABA and cytokinin regulated transcription factor, ABI4, resulted in significant increased levels of ABCB4 transcript level. However, this regulation at the transcription level does not fully explain the rapid turnover of ABCB4 rapid turnover following treatment with ABA, CK or auxin. The reduced stability of ABCB4 at the plasma membrane was reported to be regulated by sphingolipids interactions as ABCB4 was found to be accumulated in intracellular compartments following treatment with the sphingolipid biosynthesis inhibitor, FB1, or in the background of sphingolipid biosynthesis deficient mutant, *tsc10a*. A saposin-like Aspartyl Protase class A2 (APA2;At1g62290) was found to be positively regulated by ABA or CK via ABI4 and suggested to function in sphingolipids enriched membrane rafts. This information has now been used to engineer transformants wherein ABCB4 is transcriptionally and post translationally stable under stress conditions.

The Role of CslD Proteins During Polarized Cell Wall Deposition in *Arabidopsis* Root Hair Cell

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Funding: \$180,000 (2014)

PROGRAM SCOPE

The overall goal of this research proposal is to characterize the molecular machinery responsible for polarized secretion of cell wall components in *Arabidopsis thaliana*. We have used the polarized expansion that occurs during root hair cell growth to identify membrane trafficking pathways involved in polarized secretion of cell wall components to the expanding tips of these cells, and we have recently shown that CSLD3 is preferentially targeted to the apical plasma membranes in root hair cells, where it plays essential roles during cell wall deposition in these cells. The specific aims of the project are designed to answer the following objectives: (1) Examine how CSLD3 function is integrated with regard to other members of the CSLD family and other cell wall synthetic enzymes during cell wall synthesis in *A. thaliana*. (2) Determine if CSLD proteins assemble into multi-subunit complexes. (3) Characterize CSLD synthetic activity and examine the nature of the polysaccharides synthesized by these enzymes.

FY 2014 HIGHLIGHTS

1. Cyclin B turnover precedes CSLD5 accumulation during cell division. CSLD5 selectively accumulated in dividing cells. Using time-lapse microscopy we showed CSLD5 accumulation only occurred in late mitosis, and only after loss of cyclin B1. We also showed that CSLD5 was rapidly lost in the newly-formed daughter cells.
2. CSLD5 is rapidly degraded upon completion of cytokinesis. Loss of CSLD5 from cells after mitosis suggested it might be actively degraded. Using cyclohexamide to block protein synthesis, we showed CSLD5, but not other CSLD or CESA cell wall synthases, displayed rapid turnover. Degradation of CSLD5 was ubiquitin-dependent, as treatment with the 26S proteasome inhibitor, MG132, stabilized this protein.
3. Heterologous expression and detergent-solubilization of CSLD3 in yeast. To determine the enzymatic activity of CSLD proteins, we wanted to express CSLD, CESA, and CSLA proteins in heterologous systems. We have successfully expressed and detergent-solubilized CSLD3, CESA6 (glucan synthase), and CSLA9 (mannan synthase) in *S. cerevisiae*. This is a significant advancement, and will provide the foundation for testing the biochemical activities of CSLD3 and other cell wall synthases with purified components.

Research Publications (2013-2014):

- 1) Gu, F., and Nielsen, E. (2013) Targeting and Regulation of Cell Wall Synthesis during Tip Growth in Plants. *J. Integr. Plant Biol.*, 55, 835-46.
- 2) Marella H., Nielsen, E., Schachtman, D.P., and Taylor, C.G. (2013) The amino acid permeases, AAP3 and AAP6, are involved in root-knot nematode parasitism of *Arabidopsis*. *Mol. Plant-Microbe Interact.*, 26, 44-54.

- 3) Antignani, V., Szumlanski, A.L., Bak, G., Chandrasekaran, S., and Nielsen, E. (2015) RabA4b GTPase recruited effector proteins are involved in the regulation of SA-dependent PR gene expression in *Arabidopsis*. *The Plant Cell*, in press.

Two Dimensional Electronic Spectroscopies for Probing Coherence and Charge Separation in Photosystem II

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Funding: \$475,000 (2014-2015)

PROGRAM SCOPE

The basic photosynthetic architecture consists of antenna complexes to harvest solar energy and reaction centers to convert the energy into a stable charge separated state. In oxygenic photosynthesis, the initial charge separation event occurs with near unit quantum efficiency in the photosystem II reaction center (PSII RC). PSII is the only known natural enzyme that uses solar energy to split water, making the elucidation of its design principles critical for our fundamental understanding of photosynthesis and for our ability to mimic PSII's remarkable properties. This proposal focuses on key deficits in our current understanding of the PSII RC and aims to address the following open questions: 1) What is the electronic structure of the PSII RC? 2) What are the charge separation pathways in the PSII RC? 3) Does coherence facilitate charge separation in the PSII RC? To address these open questions we will apply broadband 2DES in isolated PSII RCs and in larger PSII complexes containing light-harvesting antennae, and continue development of new 2D spectroscopy methods to probe charge separation. 2DE-Stark spectroscopy will utilize an applied electric field to aid in separating excitonic and charge transfer states and enable identification of charge separation processes. These studies will enable us to further test and refine electronic structure models of the PSII RC and our description of the charge separation process. Our extensive studies of the PSII RC address the fundamental structure-function relationship in this important system to meet the grand challenge of elucidating the design principles used by nature to converting sunlight into chemical energy. The proposed studies will push the development of new methods for spectroscopic simulation and refinement of electronic structure. The newly developed experimental tools will be widely applicable to artificial light-harvesting systems, giving important experimental feedback for improving their design.

FY 2014 HIGHLIGHTS

The primary events of photosynthesis involve the absorption of light and the conversion of that absorbed energy into charge separation. This process is extremely rapid and in oxygenic photosynthesis it takes place in the photosystem II reaction center (PSII RC). Using two-dimensional electronic spectroscopy (2DES) we were able to track the energy transfer and charge separation events with exquisite time resolution. This high time resolution enabled us to see modulations in the optical signals at very specific frequencies that we identified as arising from coupled motions of the electrons and nuclei of the PSII RC. We carefully characterized these frequencies and correlated our observation of the coherent dynamics with specific electronic and mixed electronic-vibrational states of the system. We were able to reproduce the key features in our experimental data using a model that couples the key

vibrational modes identified by our experiments with specific electronic states. The simulations showed that vibrations possessing energies that match the energy gaps between the electronic states in the system strongly enhance the speed of charge separation. These observations indicate that electronic-vibrational resonances may be a key design principle of natural photosynthetic systems to promote efficient charge separation. In other progress, we have developed a new experimental implementation of 2DES that enhances the signal-to-noise-ratio. We have developed a new method to enable rapid and high signal-to-noise characterization of coherent dynamics. We have performed polarization-dependent 2DES on isolated PSII RC and PSII core complexes that contain additional CP43 and CP47 antennae. We have developed a novel dynamic Stark spectroscopy to specifically observe kinetic processes of charge separation and have collected data on the PSII RC. We are using the new array of spectroscopic data on the PSII RC to refine our model of its electronic structure.

Identification and Characterization of Glycosyltransferases Involved in the Synthesis of the Side Chains of the Cell Wall Pectic Polysaccharide Rhamnogalacturonan II

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Funding: \$170,000 (2014)

PROGRAM SCOPE

Terrestrial plants are estimated to annually assimilate at least 100 billion metric tons of CO₂ through the process of photosynthesis. Much of the resulting photosynthate is used to produce the polysaccharide-rich walls that surround plant cells. We are studying the biosynthesis and structure of rhamnogalacturonan II (RG-II), a structurally conserved pectic polysaccharide that exists as a borate ester cross-linked dimer in the primary cell walls of all vascular plants. Incomplete borate cross-linking of RG-II and mutations that lead to altered RG-II structure or cross-linking adversely impact wall assembly and function and severely impair plant growth. However, the relationship between RG-II structure, cell wall organization, and plant growth is poorly understood. Few of the genes and proteins involved in RG-II synthesis have been identified and functionally characterized. Apiose is a key component of RG-II as it links two of the four oligosaccharide side chains to the homogalacturonan backbone and is involved in borate cross-linking of two RG-II molecules. We hypothesized that UDP-apiose (UDP-Api), the activated form of apiose used in RG-II synthesis, is a key factor in controlling RG-II formation. We also hypothesized that the appearance of functional UDP-Api synthase was a critical event in vascular plant evolution. RG-II is present in the cell walls of all vascular plants, but appears to be absent in avascular plant (bryophytes) cell walls. We are using a combination of molecular, biochemical and chemical techniques to investigate UDP-Api formation in land plants and to identify glycosyltransferase involved in RG-II synthesis. We are also using NMR spectroscopy together with mass spectrometry to characterize RG-II structure and cross-linking in diverse plants. Our long-term goal is to describe features of RG-II that are important for its self-assembly into a borate cross-linked dimer and how this dimer contributes to the functions and properties of the wall.

FY 2014 HIGHLIGHTS

A UDP-Api synthase (UAS) from the duckweed which has apiose-rich cell walls, was expressed as a recombinant protein and characterized. Duckweed UAS is being used to form UDP-Api for apiosyltransferase assays. We identified two protein sequences from a seagrass with high amino acid sequence homology with duckweed UAS. A recombinant version of one of the seagrass proteins was shown to have UDP-Api synthase activity. The moss *Physcomitrella patens* contains a homolog of UAS, but a recombinant version of the protein had no UAS activity. Domain swapping studies indicate that changes in the amino acid sequence between aa 1-215 prevent the moss “UAS-like” protein from being a functional UDP-apiose synthase. In collaboration with Russell Carlson (U. Georgia) and Gary Stacey (U of Missouri), we have shown that 95% of the RG-II exists as the borate ester cross-linked dimer in the cell walls of soybean (*Glycine max*) roots and root hairs. In collaboration with Paula McSteen (U. Missouri), we have shown that borate cross-linking of RG-II is reduced by 42% in the immature tassels of the maize tassel-less1 (*tls1*) mutant. This mutant has defects in inflorescence development, and in severe cases vegetative development, similar to the effects of boron deficiency. The reduction of RG-II dimers in the *tls1* mutant tassels suggests that the defects observed in mutant plants are, at least in part, due to defects in the cell wall.

Novel Microbial Based Enzymatic CO₂ Fixation/Carboxylation Mechanisms

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Funding: \$180,000 (2014)

PROGRAM SCOPE

This project's goal is to provide mechanistic insights into novel carboxylation reactions that occur in the microbial metabolism of alkenes and ketones. In *Xanthobacter autotrophicus* Py2 (Xa), two convergent pathways have been characterized for the metabolism of these compounds. These pathways culminate in carboxylation reactions catalyzed by either acetone carboxylase (AC) or 2-ketopropyl CoM carboxylase (2-KPCC). These enzymes are mechanistically distinct and have unique cofactor requirements. Our experimental approach combines biochemical characterization and X-ray structure determination of these enzymes in the presence of their substrates, products, and inhibitors to elucidate the carboxylation mechanisms. An outgrowth of these studies is our investigation of the Xa CoM biosynthetic pathway. The requirement for CoM in this metabolic pathway was unexpected, as it was previously thought that CoM was used only by methanogens. The AC carboxylation reaction does not utilize biotin and is ATP dependent. AC is unusual among carboxylases as its mechanism results in hydrolysis of ATP to 1 mol AMP and 2 mol of Pi. Previous studies suggest that ATP hydrolysis is coupled to both the activation of acetone to form a phosphoenolacetone intermediate and the activation of bicarbonate to carboxyphosphate. These studies suggest that acetone carboxylase is a fundamentally new class of carboxylase. Our crystal structure of 2-KPCC shows CO₂ in the active site, ideally positioned for electrophilic attack on the hypothetical enolacetone intermediate to yield acetoacetate. Kinetic studies show a side reaction occurs in the absence of CO₂ in which protons substitute as the attacking electrophiles yielding acetone instead of acetoacetate. We are using kinetics, mutagenesis and x-ray

crystallography to determine how 2-KPCC discriminates between CO₂ and protons as substrate electrophiles.

FY 2014 HIGHLIGHTS

We have purified recombinant AC from Xa, *Aromatoleum aromaticum* (Aa), and *Azotobacter vinelandii* (Av). Our data shows AC occurs in two variants which differ in ATP stoichiometry. For Xa, one ATP is consumed per acetone; for Aa and Av, two ATP are consumed. Phylogenetic analysis supports this distinction: we have shown that AC from Xa lies on a different clade than AC from Aa and Av. Our kinetic studies have identified that the reaction proceeds through a phosphorylated isopropene intermediate. Structural characterization of AC is ongoing; we have Xa crystals that diffract to ~3Å and crystallization conditions are being optimized for Xa, Aa, and Av. We hypothesize that several features surrounding the 2-KPCC active site may affect substrate discrimination: the N- and C-termini, a cis-proline flanked loop and a hydrophobic pocket encapsulating the CO₂ substrate. We are assessing the impact of CO₂ concentrations on carboxylation in wild-type 2-KPCC. Analysis of 2-KPCC variants is underway. We have purified a 2-KPCC variant with the cis-proline loop deleted. Other variants to be constructed include deletion of both termini, and mutation of CO₂ binding site residues. A gene cluster near the epoxide carboxylase pathway is implicated as the putative CoM biosynthetic operon in Xa. To define the biosynthetic intermediates, we have cloned the putative operon and individual ORFs for expression in *E. coli*. One of these ORFs, *xcbE1*, is homologous to D-cysteine desulfhydrases, a group of PLP-dependent enzymes that extract sulfur from D-cysteine and produce pyruvate, H₂S and ammonium. Kinetic studies are underway using purified recombinant XcbE1. Supplying XcbE1 with cysteine yields H₂S and pyruvate. Our kinetic data show that XcbE1 does not have a strict preference for L- or D-cysteine, unlike its homologs that do not catalyze a reaction in the presence of L-cysteine.

Enzymology of Methanogenesis: Mechanism of Methyl-Coenzyme M Reductase

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

The goal of this project is to determine the enzymatic mechanism of methyl-CoM reductase (MCR), the key enzyme in the synthesis of methane, which is the primary constituent of natural gas and accounts for 22 percent of the energy consumption of the U.S. This enzyme is responsible for more than 90% of the earth's atmospheric methane. MCR catalyzes the formation of methane and a heterodisulfide (CoB-S-S-CoM) from methyl-Coenzyme M (methyl-CoM) and Coenzyme B (HSCoB). There is controversy about whether methane is formed via methyl-Ni(III) or methyl radical intermediates. By using substrate analogs and MCR variants, we have trapped reaction intermediates in the catalytic cycle to resolve this controversy. We also are attempting to determine the crystal structure of the Ni(I) state of MCR and the structures of catalytic intermediates in the catalytic cycle. We also are determining how MCR is activated *in vivo*. Protocols have been developed to activate MCR for performing mechanistic studies; however, we do not yet know how MCR undergoes activation in the cell. We have recently discovered

that CO and CODH can replace H₂ and hydrogenase in the cellular activation system. Thus, we are in an excellent position to determine the common cellular pathway for activation of MCR by H₂ and CO.

FY 2014 HIGHLIGHTS

Transient kinetic studies of the MCR-catalyzed reaction of methyl-SCoM with CoB6SH, a CoBSH analog lacking one methylene group in the heptanoyl group, suggest a new MCR mechanism involving conversion of Ni(I) to a Ni(III) intermediate (MCRox1) in a reaction tightly coupled to methane formation. Transient and steady-state kinetic studies of the MCR reaction with native substrates allowed definition of each of the individual steps in the MCR reaction along with their rate constants. This will represent the first published transient kinetic study of active MCR with its native substrates. These studies suggest a novel mechanism by which MCR, which uses an ordered BiBi ternary complex mechanism, dictates a strict order of substrate binding (methyl-SCoM first, CoBSH second), required for the chemical reaction. While some enzymes prevent binding of the “incorrect/second” substrate to the free enzyme and recognize only the “correct/first” substrate, MCR can form a binary complex with either substrate. It appears to couple binding of methyl-SCoM to expulsion of any pre-bound CoB7SH from its nonproductive binding mode. It also uses conformational energy to promote CoB7SH binding to the productive binary complex and to effect the synergetic movement of substrates in position for the chemical reaction. Activation energies for each step in the MCR reaction have been determined by presteady-state and steady-state kinetics. These are serving as input parameters for computational studies of the MCR mechanism.

Understanding the Role of the Exocyst in Regulating the Dynamics of Vacuole Trafficking and Secretion

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Funding: \$555,000 (2014-2016)

PROGRAM SCOPE

Enhanced mobilization of vacuolar cargoes by: 1) Defining cellular mechanism(s) involved in uptake/compartimentalization/mobilization of energy-relevant nutrients and soluble/membrane proteins. 2) Defining genes for mobilization of reserves in vacuoles of vegetative/seed tissues. 3) Understand how reserves/proteins/metabolites are partitioned dynamically between vacuoles and sites of intra/extracellular use. 4) Improving biomass/yield/fitness by efficient storage and utilization of energy-rich stores. We will use plasma membrane (PM) proteins such as the auxin transporter PIN₂ which controls vacuolar trafficking via auxin and will serve as vesicle markers to the vacuole and PM to study trafficking dynamics. Goals will contribute to biomass as renewal energy via knowledge/tools to manipulate vacuolar trafficking. Due to reduced funding, we focused on bioactive chemical ES2 and its target, the exocyst.

Objective 1. Understand the exocyst in regulating vacuole trafficking. We hypothesize the exocyst is part of a mechanism controlling dynamics of vacuole trafficking and exocytosis. As a separate chemical biology approach with non-DOE seed money, we screened for chemicals perturbing endomembrane trafficking, including aberrant targeting to the vacuole. Our early data indicates the cognate target of the chemical ES2 as the exocyst protein EXO70A1 which may regulate vacuole targeting and exocytosis. This

is an opportunity to understand regulation of vacuole trafficking by dissecting the role of EXO70s/exocyst.

Objective 2. Determine the structure of EXO70A1 and map ES2 binding domains. We hypothesize that the ES2 binding site will reveal regions regulating vacuole trafficking and exocytosis. Our results will provide insights into mechanisms enabling biotechnology to enhance efficiency of protein/carbohydrate storage in vacuoles.

FY 2014 HIGHLIGHTS

During this review period we have achieved the following towards our program goals:

1. An EXO70 protein with a C-terminal truncation resulted dominant ES2 resistance, uncovering possible distinct regulatory roles for the N-terminus and C-terminus of the protein. We have been using this mutant as a starting point to uncover novel features of the exocyst and its role in regulating the dynamics between targeting of key metabolites to the vacuole vs. plasma membrane (PM).
2. Utilizing the bioactive compound ES2 we identified its cognate target as the EXO70A1 subunit of the exocyst complex which is necessary for exocytosis and is highly conserved. This was done using a combination of genetics and chemical proteomics. We have recently demonstrated by NMR that ES2 physically interacts with EXO70 from *Arabidopsis* and mouse indicating that conserved nature of the binding site. Mutations in the plant EXO70 subunit reduce binding interaction.
3. We have shown that the compound affects the polar targeting of EXO70 and FRAP shows that the compound inhibits the plasma membrane association of the EXO70 subunit of the exocyst.
4. We have been working towards the crystal structure of *Arabidopsis* EXO70A1 and have been able to obtain high quality crystals that can be used to determine structure in the presence or absence of ES2. This will be the first plant EXO70 structure to be reported.
5. To the extent of our knowledge, there are no other compounds known to target the exocyst. Beyond our studies to understand the regulation of vacuole vs. PM targeting of vacuole and other cargoes from the viewpoint of improved energy reserves for plant biotechnology, exocyst function have been linked to diabetes and even some cancer. So the target site may be novel and could provide a drug lead for increased human health.

EARLY CAREER: Engineering Self-Assembled Bioreactors from Protein Microcompartments

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Funding: \$159,224 (2014)

PROGRAM SCOPE

Biological systems use organization to segregate incompatible processes. Many metabolic pathways are confined to specific organelles to insure pathway fidelity, catalyzing reactions out of chemical equilibrium within the cell, and limiting pathway toxicity. However, the ability to spatially organize important processes *in vivo* remains a major challenge to the field of biological engineering. A reliable method for constructing spatial organization in the form of a synthetic organelle would be useful in metabolic engineering, where it could be used to improve the rate and yield of biochemical reactions.

One biological assembly that could form the basis of a synthetic organelle is the bacterial microcompartment (BMC). BMCs are enzyme-containing complexes that catalyze reactions unfavorable to the host. They have a modular structure and consist of self-assembling shell proteins and packaged, targeted enzymes. Many of the genes required for BMC assembly have been identified, and recent genetic manipulations suggest that BMC are suitable for engineering. We propose experiments to define the assembly process of BMCs, identify the BMC components sufficient for function, and to develop synthetic organelles capable of catalyzing a model pathway. Our goals are:

Aim 1: To define BMC assembly and function within cyanobacteria. How BMCs function *in vivo* is poorly defined. Here, we will use a model BMC to define the nature and mechanism of particle formation and degradation. We will also probe the interplay between BMC function and cellular growth and metabolism *in vivo*.

Aim 2: To develop a model BMC for synthetic biological applications. We will apply our understanding of BMC assembly and function to the long-term goal of creating synthetic organelles. We will develop a minimal and modular BMC chassis for further protein engineering. We will then define how proteins are targeted to BMCs and use this as a means of creating a novel BMC capable of catalyzing ethanol fermentation.

FY 2014 HIGHLIGHTS

The goal of our work is to develop an understanding of how proteinaceous bacterial microcompartments (BMCs) assemble and function in their *in vivo* context and to use this knowledge for the rational engineering of compartments with novel catalytic properties. This proposed work is broken down into two major aims: i). To probe assembly and function of using the cyanobacterial model BMC system (i.e. the carboxysome) from *Synechococcus elongatus* PCC7942 developed in my postdoctoral work and ii). Develop and engineer a heterologous carboxysome (CB) expression system based upon the CB regulon from *Halothiobacillus neapolitanus* (HnCB). Briefly, the major advances during the 2013-2014 funding period are the following:

1. Developed optimal instrumentation for live-cell cyanobacterial imaging.
2. Begun to tease apart the mechanism of carboxysome assembly, the initial results of which were published (Chen *et al.* PloS One 2013).
3. Discovered the stringent response my control polyphosphate and, ultimately, photosynthetic carbon fixation in cyanobacteria.
4. Deciphering the mechanism of CB assembly in the model *Halothiobacillus*.
5. Exploring thermophilic 'nanocompartment' encapsulins in *E. coli* as an alternative to microcompartments.

Molecular and Genetic Basis of Sodium/Potassium Transport and Distribution in Plants

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Funding: \$179,565 (2014)

PROGRAM SCOPE

Salinity stress is progressively detrimental to renewable bioenergy capture and storage in plants and interferes with photosynthetic activity and metabolism. Sodium (Na^+) is toxic to most plants at high concentrations. Elucidation of the fundamental basic molecular and biophysical mechanisms underlying Na^+ uptake and distribution throughout plant tissues and cellular organelles can lead to new approaches for enhanced energy capture and storage in plants. Our DOE supported research has identified the AtHKT1;1 transporter and revealed that it constitutes a key mechanism for protection of plants from salinity stress by excluding toxic alkali-metal sodium (Na^+) ions from leaves. Recent mapping of salinity resistance quantitative trait loci (QTL) in grasses, and analyzing candidate HKT genes in rough mapping domains suggest that analogous HKT transporter-mediated salinity tolerance mechanisms that the P.I.'s lab has identified in *Arabidopsis* are key salinity resistance mechanisms in grasses. Our DOE research focuses on the basic biophysical, physiological, and regulatory mechanisms through which HKT sodium cation transporters and Potassium (K^+) transporters play central roles in mediating salt tolerance in plants. Chloroplast transporters are predicted to be of key importance for efficient photosynthesis. However, the genes encoding many chloroplast transporters, including the molecular K^+ transport mechanisms across chloroplast membranes, remain unknown. Our research is identifying and characterizing chloroplast-targeted K^+ transporters and determining their roles in plant growth, chloroplast function, and salinity responses.

FY 2014 HIGHLIGHTS

The molecular identity and the fundamental functions of transport proteins facilitating K^+ transport across the chloroplast envelope membranes remained unknown. Our analyses of prokaryotic organisms indicated members of the KEA family as candidates. To address overlapping gene functions, we designed and developed artificial microRNAs (amiRNAs) on a genome-wide scale in *Arabidopsis*. Since no loss-of-function mutants had been identified in K^+ transporters that affect chloroplast function and photosynthesis, we used amiRNAs and found that co-knock-down of KEA1 & KEA2 gives rise to plants with a decreased maximum efficiency of photosystem II (Fv/Fm) determined by pulse amplitude modulated (PAM) measurements of whole rosettes in the P.I.'s lab (Kunz *et al.*, 2014 PNAS). We found that KEA1 and KEA2 proteins are targeted to the inner envelope membrane of chloroplasts, while KEA3 is targeted to the thylakoid membrane. *kea1kea2* double mutants, but not single mutants, showed impaired photosynthesis in young plants and pale green leaves. The pH component of the proton motive force across the thylakoid membrane was found to be significantly decreased in *kea1kea2* plants. Electron microscopy of leaf cells revealed swollen chloroplasts, dramatically reduced chloroplast starch levels, disrupted envelope membranes and reduced thylakoid membrane density (Kunz *et al.*, 2014). Unexpectedly, exogenous NaCl application reversed these phenotypes via a proposed osmotic stabilization. Furthermore, the *kea1kea2* background enabled genetic analyses of the functional significance of other chloroplast transporters using higher order mutants: *kea1kea2 Na⁺/H⁺ antiporter1 (nhd1)* and *kea1kea2kea3* triple mutants showed an enhanced impairment in photosynthesis (Kunz *et al.*, 2014). Taken together, our characterization of the plastidial inner envelope KEA1&2 transporters demonstrates their fundamental roles in chloroplast osmoregulation, integrity, and chloroplast pH regulation.

Reduction of CO₂ to Hydrocarbons Catalyzed by Nitrogenase Will Be Investigated

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Funding: \$190,000 (2014)

PROGRAM SCOPE

The research objectives of this project are to gain a molecular level understanding of the activation and reduction of CO₂ to hydrocarbons catalyzed by the bacterial enzyme nitrogenase. Nitrogenase normally catalyzes the multi-electron/proton reduction of dinitrogen (N₂) to two ammonia (NH₃). We have discovered that the protein surrounding the active site metal cluster, FeMo-cofactor, can be remodeled, allowing larger compounds to become substrates for nitrogenase. In one such remodeled nitrogenase, we were able to demonstrate that nitrogenase could reduce CO₂ by 8 electrons/protons all the way to methane (CH₄) in a catalytic reaction unprecedented in biology. Our goals are to understand these reactions and to improve the reactions through further remodeling of the active site of nitrogenase.

FY 2014 HIGHLIGHTS

We have made significant advances in our understanding of the metal hydrides at the active site that are certainly involved in CO₂ reduction to hydrocarbons in the remodeled nitrogenase. The state of our understanding was presented in a Chemistry Review paper that appeared in early 2014. We also have made good progress using isotopes to understand the rate limiting steps in the multi-step reduction of CO₂ to hydrocarbons.

Nanotube-Supported Phospholipid Bilayers

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

The overall long term objective of this project is to develop a new class of nanoscale biotechnological objects - substrate-supported lipid nanotubes - and to utilize these nanoscale structural elements for building robust hybrid biological nanodevices that are based on functionally active membrane proteins. Specifically, we aim at: (1) developing efficient experimental protocols for loading and self-assembling bilayer membranes of various lipid compositions inside the nanochannels formed in anodic aluminum oxide (AAO) substrates; (2) improving technology for fabricating homogeneous AAO with desired pore dimensions and low light absorbance to enable biophysical studies of light-harvesting biomolecular systems; (3) investigating effects of surface chemistry on the lipid self-assembly and the properties of the lipid bilayers formed by surface modification of nanoporous substrates; (4) demonstrating initial feasibility of employing lipid nanotube technology for building hybrid nanostructures based on membrane proteins. The ultimate outcome of the program will be experimental methods and protocols for building robust functional hybrid nanostructures that could be used for biomimetic solar energy conversion and/or bioinspired energy transduction and separation technologies.

FY 2014 HIGHLIGHTS

- 1) Developed centrifugation-based method and accessories to increase loading of lipid bilayers into AAO nanochannels by at least twofold regardless the phospholipid composition.
- 2) Developed and optimized a number of high throughput procedures for fabricating high quality nanoporous substrates with pore diameters ranging from 25 to 90 nm and exceptionally narrow (4 to 5 nm) pore diameter distributions.
- 3) Developed nanoporous substrates that are transparent at wavelength above 260 nm for biophysical studies of light-harvesting biomolecular systems.
- 4) By using lipid nanotube technology showed that the Pf1 helix tilt angles in two lipid systems are not entirely governed by the membrane thickness but could be rationalized by hydrophobic interactions of lysines with lipids at the bilayer interface.
- 5) Carried out initial experiments on incorporating rhodopsins into lipid nanotubes formed inside macroscopically aligned ceramic nanoporous substrates for NMR and EPR structural studies as well as for biosensor applications.

Engineering Selenoproteins for Enhanced Hydrogen Production

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Funding: \$160,000 (2014)

PROGRAM SCOPE

Hydrogenases are crucial enzymes in the production and utilization of hydrogen, a possible fuel of the future. A fundamental understanding of the function of these redox enzymes is required to make biogenic hydrogen production a viable fuel source. The element selenium is found in a subset of hydrogenases that have greater catalytic power than their sulfur-containing homologs. Selenium is found in proteins in the form of selenocysteine (Sec), an amino acid in which a selenol group replaces the thiol moiety of cysteine. It is thought that the unique catalytic potential of selenium is required for certain redox enzymes to function in their native environment (e.g., glutathione peroxidase in mammals or formate dehydrogenase in bacteria). Some organisms (e.g., methanogens) simultaneously contain homologous [NiFe] hydrogenases with either Sec or cysteine in their catalytic center. In [NiFeSe] hydrogenases, the selenium always coordinates the Ni atom in the metal cluster and three cysteines complete the coordination shell surrounding the NiFe center. The reason for this evolutionarily conserved structural arrangement and the answer as to how Sec enhances the catalytic potential of hydrogenases and other redox enzymes remains unknown. The versatile amino acid Sec is formed by the conversion of serine while attached to tRNA^{Sec} resulting in Sec-tRNA^{Sec}. Sec is co-translationally inserted into proteins directed by a UGA codon in the mRNA; a special tRNA^{Sec} and a particular mRNA structure-mediated recoding event are involved in this process. Given this precise recoding mechanism, mutagenesis methods to generate proteins where Sec is inserted at any desired position are currently unavailable. The aim of this proposal is (1) to develop a method that will make protein design and engineering with selenocysteine feasible, and (2) to use this method to enhance the activity of hydrogenases by conversion of critical active site cysteine residues to selenocysteine.

FY 2014 HIGHLIGHTS

Aim 1: By designing a synthetic tRNA^U (a tRNA^{Sec} that is recognized well by elongation factor Tu) and by evolving from wild-type EF-Tu the variant EF-Sel (with improved recognition properties of Sec-tRNA^U) we have generated a translation system that can generate any desired selenoprotein in *E. coli* with high specificity and yield.

Aim 2: We have chosen the *Methanocaldococcus jannaschii* [Fe]-hydrogenase Hmd as a model protein to convert its active site cysteine (position 176) to selenocysteine. Expression of an HmD gene containing UAG as codon 176 in *E. coli* with our UTu system (see Aim 1) yielded a Sec-containing Hmd protein in good yield (2-3.5 mg/L culture). Sec incorporation was confirmed by LC-MS/MS analysis. Biochemical characterization of this selenoenzyme will be carried out in the laboratory of Dr. Rudolf Thauer, Marburg, Germany.

Plant Response to LCO/CO Signals

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

Plants are sessile organisms and, therefore, have evolved complex mechanism by which they sense and respond to their external environment. Chitooligosaccharides (CO), released from pathogen fungi, induce plant innate immunity while, in legume plants, lipo-chitooligosaccharides (LCO) induce the establishment of the nitrogen fixing symbiosis with rhizobia. Our project seeks to understand how very similar signals (CO and LCO), recognized by similar LysM receptor-like kinases, can elicit such different plant responses. For example, recently we elucidated the heterotetrameric structure of the CERK1-LYK5 CO receptor complex, which is very similar to the LCO receptor. It has been the dream for many years to leverage knowledge about the rhizobial-legume symbiosis to develop similar symbioses with non-leguminous plants (e.g., corn). Until recently, it was thought that non-legumes cannot form such a symbiosis due to an inability to recognize and react to the LCO signal. However, we recently showed that many non-legumes, perhaps all, do recognize the LCO but this result in a suppression of innate immunity and not symbiosis. Indeed, we hypothesized that this role of LCO may have predated its symbiotic function to promote infection by the bacterium. CO and LCO signals trigger the release of extracellular ATP by the plant, which may also act as a signal; a role that is well documented in animal systems. We recently identified the first plant receptor for eATP, DORN1 (doesn't recognize nucleotides). Mutants defective in *dorn1* do not react to ATP addition. There is a significant overlap between the genes induced by ATP and those induced by CO addition, as well as treatment with a variety of biotic and abiotic stressors. The data suggest that eATP is a previously overlooked, critical signal that explains a significant amount of the gene expression previously assigned strictly to the stress treatment.

FY 2014 HIGHLIGHTS

Adenosine 5'-triphosphate (ATP), the universal energy currency of all organisms, is released into the extracellular matrix and serves as a signal among cells, where it is referred to as an extracellular ATP (eATP). In mammals, eATP is perceived by plasma membrane P2-type purinoceptors. However, similar ATP receptors do not exist in plants, although extracellular ATP has been shown to play critical roles in plant growth, development, and stress responses. Recently, we identified the first plant receptor for extracellular ATP, DORN1, by isolation of an *Arabidopsis thaliana* mutant that failed to show an intracellular calcium response upon ATP addition (Choi *et al.*, 2014). DORN1 encodes a legume-type lectin receptor kinase (i.e., lectin receptor kinase I.9; At5g60300) that is structurally distinct from the mammalian extracellular ATP receptors. DORN1 binds ATP with high affinity (K_d : 45.7 ± 3.1 nM), as well as other nucleotides, and is required for ATP-induced calcium response, MAPK activation, and gene expression. Ectopic expression of DORN1 increased the plant response to physical wounding. We propose that DORN1 is essential for perception of extracellular ATP and likely plays a variety of roles in plant stress resistance.

Choi, Jeongmin, Tanaka, Kiwamu, Cao, Yangrong, Xi, Yue, Qiu, Jing, Liang, Yan, Sang Yeol Lee, Stacey, Gary (2014) Identification of a plant receptor for extracellular ATP. *Science* Vol. 343 no. 6168 pp. 290-294

Regulation of Actin Stochastic Dynamics: Single Actin Filaments as Tracks for Delivery of Materials to the Cell Wall

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Funding: \$350,000 (2014-2015)

PROGRAM SCOPE

Plant cell walls represent the largest renewable source of carbon for use in biofuel production. Maximizing extraction of wall-stored carbon for industrial purposes requires a detailed understanding of polysaccharide composition, biophysical properties, and assembly mechanisms. Understanding how, how much, and where noncellulosic polysaccharides are delivered and incorporated into walls is a major knowledge gap which currently impedes efficient use of biomass for biofuels. In plants, a cytoplasmic network of dynamic filamentous structures, the actin cytoskeleton, functions as tracks or highways for long-distance transport. Although it is widely believed that actin provides the transportation infrastructure to deliver matrix polysaccharides and biosynthetic enzymes to the PM and cell wall, there is little direct evidence to this effect. Using state-of-the-art fluorescence imaging methods, we have previously described the dynamic remodeling of actin filament arrays in living plant cells and quantified key properties of individual filament turnover. Moreover, we have established genetic control over actin filament dynamics by overexpressing and downregulating several actin-binding proteins. One such player, capping protein (CP), modulates the availability of filament ends and controls filament length and lifetime. We predict that the single filaments serve as highways for secretory vesicle traffic; thus, when these tracks are long and long-lived, cargo delivery is most efficient. Therefore, we will test the central hypothesis that single actin filament lengths and lifetimes regulate exocytosis, thereby controlling the rate of deposition of matrix polysaccharides and the delivery of cell wall biosynthetic

enzymes to the PM. Our objectives include: 1) establishing whether single actin filaments serve as tracks for trafficking of matrix polysaccharides and cell wall biosynthetic enzymes; and 2) testing whether filament length and lifetime alter exo- and endocytosis.

FY 2014 HIGHLIGHTS

- We demonstrated that overexpression of *Arabidopsis* capping protein (CP OX) has the opposite cell expansion and cytoskeletal phenotypes compared to cp knockdown lines. Specifically, CP OX lines have reduced axial cell expansion in etiolated hypocotyls as well as less dense cytoskeletal arrays. Changes to single filament turnover in CP OX lines results in actin filaments with reduced annealing frequency, shorter maximum length and decreased lifetime. This work was published in *Molecular Biology of the Cell*.
- We performed subcellular fractionation, sucrose-density gradient separations and immunocytochemistry to establish that CP is a membrane-associated protein and associates with endomembranes such as Golgi. This work was published in *Plant Physiology*.
- We established collaborations to determine cell wall composition in cp mutants and showed that crystalline cellulose content was significantly reduced compared to wild-type plants, in preliminary experiments. We also analyzed monosaccharide content in cp and found an increase in xylose and fucose, whereas total glucose was essentially unchanged compared to wild type. This is consistent with an increased xylan content in cpb-1 walls. In contrast, arabinose and galactose content decreased significantly, suggesting a reduction in pectin or arabinogalactan proteins.

Molecular Mechanism of Energy Transduction by Plant Membrane Proteins

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PROGRAM SCOPE

The plasma membrane is the point of contact between a cell and its external environment and plays a critical role in the growth and development of all organisms. The proteins within this membrane that act as pumps, carriers, and channels together convert the chemical energy of ATP into gradients of organic and inorganic solutes that support life. In higher plants and fungi, foremost among these transport proteins is the proton pump (H^+ -ATPase) since it alone generates the proton motive force (composed of both a transmembrane electrical potential and a proton chemical gradient) that drives the transport of solutes essential for cell growth. A unique aspect of this enzyme is its ability to generate very large membrane potentials and a low extracellular pH whose magnitude is regulated by changes in light, hormones and other environmental perturbations such as drought and salt stress. The overall research goal of this project is to use genetic and chemical technologies for understanding the molecular structure and function of this protein, both in terms of what precise physiological and developmental roles it is playing in everyday plant life, as well as in learning how it converts chemical energy into electrical energy and how this process is tightly regulated. Our specific approach is to mutagenize the gene encoding this enzyme either in intact *Arabidopsis* plants or in yeast, and study the resultant phenotypes. A major recent focus has been on identifying posttranslational modifications and

interacting partners of the enzyme, and substantial progress has been made in developing and using the tools required for understanding the role of kinase-mediated phosphorylation.

FY 2014 HIGHLIGHTS

In *Arabidopsis* and all other plants, this protein is encoded by a family of 11 genes called AHA (*Arabidopsis* H⁺-ATPase)'s. AHA1 and AHA2 appear to be functionally redundant and together produce mRNA and protein corresponding to ca. 70% of the enzyme found in plant extracts. In previous years we performed a comprehensive study of the effects of genetically reduced plasma membrane proton pump activity for AHA1 and AHA2. We have recently used a system for obtaining a translationally fused 'tagged' pump that, importantly, rescues growth of the lethal double mutant and allows us to readily purify the enzyme from plants treated for short periods of time with various effectors. In addition to the well-known penultimate threonine at the carboxy terminus, we have recently identified other serine and threonine residues in the protein whose phosphorylation status regulates this enzyme in response to a peptide hormone known as RALF (Rapid Alkalinizing Factor). With the tagged enzyme and isotope-assisted methods for quantitation with tandem mass spectrometers, we are measuring posttranslational changes in the ATPase and elucidating how these affect the three dimensional structure and catalytic functions of this critical energy transducing protein.

Endomembrane Cation Transporters and Membrane Trafficking

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PROGRAM SCOPE

A long-range goal is to understand how plants regulate cation and pH homeostasis of intracellular compartments which form the dynamic endomembrane system of all eukaryote cells. Emerging evidence indicates that distinct physico-chemical environment of endomembrane compartments is important for protein sorting, membrane trafficking, osmoregulation, signaling and possibly the synthesis and remodeling of plant cell walls. However, specific transporters involved in altering ion balance, pH or both of intracellular compartments in plant cells are poorly understood. We had uncovered a subfamily of predicted cation/H⁺ exchangers (CHX) that are prevalent in higher plants, but rare or absent in metazoans. Studies in yeast and plants indicate that CHXs members are distinct in function from the better-studied NHX1-related members some of which are also localized to endomembranes. *Arabidopsis* CHX20 in guard cell is important for stomatal opening, and two other CHXs affect the guidance of pollen tubes, whereas the functions of four AtCHXs in roots are not well-defined. Based on localization and mutant analyses, we hypothesize that CHXs modulate the ion balance, pH or both in micro-regions of endoplasmic reticulum, endosomes and prevacuolar compartment (PVC), and so affect signaling and membrane trafficking resulting in altered osmoregulation in guard cells and polar tip growth of pollen tubes.

FY 2014 HIGHLIGHTS

Two papers are being prepared for publication.

1. Role of CHX17-19 genes in reproduction and seed development. Analyses of triple mutants show that one of three homologous genes, CHX17, CHX18 or CHX19, is critical for male fertility. Although triple mutant pollen tubes grow a bit slower than Wt pollen, they target and enter ovules. Yet half of the targeted ovules per pod fail to develop into seeds and appear unfertilized. Moreover, a fraction of ovules within each pod are fertilized, though embryo development is delayed when mutant pistil is pollinated by mutant pollen. Results suggest that CHX17, 18 or 19 activity is critical for successful fertilization and the development of embryo and endosperm.
2. Modeling and mutagenesis reveal the active core in a plant cation/proton exchanger CHX17. By generating a 3D model of CHX17 using known crystal structures of bacterial Na/H antiporters, we identified potential residues involved in cation binding and transport. Results from mutagenesis experiments support a model of a cation/H⁺ exchanger with a four-helix bundle where the active core is located near the discontinuous alpha-helices of TM4 and TM11. Three dimension modeling also revealed a universal stress protein-like domain at the C tail. Taken together, our studies suggest that pH and stress conditions could regulate cation and pH homeostasis and so alter plant reproduction and seed development.

Photosynthetic Energy Capture, Conversion and Storage: From Fundamental Mechanisms to Modular Engineering

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PROGRAM SCOPE

We are conducting a highly interactive, multidisciplinary research program that addresses fundamental questions concerning the capture, conversion and storage of solar energy by photosynthetic organisms. The issues tackled are complex in nature, ranging from addressing both long-standing and emerging questions in photobiology, to developing first principles enabling rational design of cellular and subcellular modules for enhanced carbon fixation and high-energy redox reactions. The research program focuses on three major themes—"Robust Photosynthesis in Dynamic Environments," "Integrating Energy Status, Growth, and Energy Deposition," and "Characterizing and Engineering Subcellular and Cellular Modules for Photosynthetic Productivity"—that comprise multiple interrelated lines of research. The core research group includes 14 faculty members who bring a broad spectrum of formal training, basic research interests, and experimental expertise to the program, and a team of talented postdoctoral research associates, graduate research assistants, and research technicians. The program includes the development and use of novel high-throughput, non-invasive phenotyping technologies—the Dynamic Environmental Phenotyping Imager (DEPI) and the Environmental Photobioreactor (ePBR)—that enable investigators to monitor an array of fundamental photosynthetic properties and growth in dynamic environments. In addition, the program includes a series of forward-looking lines of investigation to understand the structural and biochemical bases of energy-storing modules using rational, engineering-based approaches. We anticipate that the data and technologies

resulting from the proposed research will have substantial impact on photosynthesis and related energy research as they are disseminated to the larger scientific community.

FY 2014 HIGHLIGHTS

In the “Robust Photosynthesis” project, we developed a series of new enabling technologies for high throughput measurements of photosynthetic phenotypes under dynamic environmental conditions, including new instrumentation and software platforms, and used these resources to advance our understanding of: the mechanisms of photosynthetic responses to fluctuating environmental conditions (light, temperature, humidity); the roles for the chloroplast proton motive force in regulating the photosynthetic apparatus; the importance of Golgi, ER and peroxisomes in maintaining robust plant growth; the effects of antenna composition on fitness and productivity in cyanobacteria and algae; and the role of light-quality in regulating photosynthesis, physiology and morphology in plants and cyanobacteria.

In the “Integrating Energy and Growth” project, we developed a new model that describes how photosynthetic products are partitioned to various organs of the model plant *Arabidopsis*, and made the unanticipated finding that large increases in leaf area growth, and thus light capture capacity, can result from small reductions in carbon partitioning to leaf thickness. In addition, we identified regulatory proteins with key roles in controlling the partitioning of carbon between growth and defense in *Arabidopsis* and obtained further evidence that carbon sink strength regulates photosynthetic efficiency in cyanobacteria.

Finally, in the “Modules for Photosynthetic Productivity” project, we are breaking down the complexity of photosynthesis into multiprotein modules that carry out light-harvesting or form cellular “nanoreactors” that fix CO₂. By determining the detailed structures of specific proteins that make up these modules, we have identified novel features that underlie function and are informing our design of new types of modules to enhance photosynthetic productivity.

Molecular Dissection of the *Arabidopsis* Holo-26S Proteasome

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Funding: \$180,000 (2014)

PROGRAM SCOPE

The 26S proteasome is an ATP-dependent protease complex responsible for degrading many important cell regulators in plants, especially those targeted by ubiquitylation. Its 64 or more subunits generate two subparticles: a 20S core protease (CP) that houses the proteolytic active sites and a 19S regulatory particle (RP) that binds to both ends of the CP and recruits appropriate substrates for breakdown. It has become clear that the currently defined proteasome actually represents the nucleus of an even more elaborate and dynamic particle harboring multiple routes for substrate recognition and sophisticated mechanisms to control its assembly, function, and turnover. The goal of this project is to better define 26S proteasome function and diversity by a thorough description of the particle from *Arabidopsis* using reverse genetics combined with mass spectrometric (MS) analyses of affinity-purified proteasomes. Specific goals are to: (i) define the functions of many of its core subunits, (ii) identify various accessory

proteins that aid in assembly and regulate substrate specificity, (iii) study alternative proteasomes generated by the combinatorial assembly of individual paralogs for many subunits, (iv) define how proteasomes are regulated by post-translational modifications including ubiquitylation, (v) confirm our hypothesis that the 26S proteasome is recycled by autophagy, and (vi) define the proteasome-stress transcriptional regulon that coordinately adjusts synthesis to meet proteolytic demand. Taken together, this project should reveal how the population of 26S proteasomes in particular, and protein turnover in general, are used by plants to regulate their growth, development, and responses to environment. By exploiting this knowledge, we hope to develop strategies to manipulate proteasome levels and functions to benefit agricultural yield, the growth of crops under adverse environments, and the production of renewable biofuels.

FY 2014 HIGHLIGHTS

In 2014, we generated a battery of essential tools and completed a number of objectives. We developed transgenic *Arabidopsis* plants and affinity methods to separately isolate the CP and RP subparticles based on individual isoforms. MS analyses of these seedlings detected a number of interacting factors, including a set of assembly chaperones, including PBAC2, PBAC3 and UMP1 for the CP, and ECM29, NAS2, NAS6, and HSM3 for the RP. We also detected two new factors that likely represent here-to-fore unknown CP chaperones. By MS analysis of isoform-specific particles, we observed the random incorporation of isoforms into 26S proteasomes, indicating the likelihood that distinct proteasome subtypes are not deliberately assembled by plants. By transcriptome studies on *Arabidopsis* deficient in active proteasomes, we identified an extensive regulon impacted by proteasome stress, which includes core and accessory components of the 26S proteasome, assembly chaperones, heat shock proteins, oxidative-stress responsive factors, and a number of transcription factors. Through co-expression, protein interaction, and promoter element studies, we identified a common cis DNA element that binds the NAC-type transcription factors NAC53 and NAC78, that is, at least, partially responsible. Studies with nitrogen-starved and proteasome-inhibited plants revealed that proteasomes are also rapidly removed by autophagy. This inhibitor-induced proteophagy is concomitant with extensive ubiquitylation of the proteasome and involves the ubiquitin receptor RPN10 that also exists in a free form in addition to its integration into the RP subparticle. By simultaneously interacting with ubiquitylated proteasomes and lipidated ATG8 lining the enveloping autophagic membranes, RPN10 helps sequester and transport damaged proteasomes to the vacuole.

Proteomic Study of Brassinosteroid Responses in *Arabidopsis*

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Funding: \$160,000 (2014)

PROGRAM SCOPE

The goal of this research project is to understand the molecular and cellular mechanisms that control plant growth. Specifically, this project uses proteomic approaches to identify cellular proteins that respond to the growth-promoting hormone signal, brassinosteroid, and that contribute to cell growth processes such as cell wall synthesis, secretion of cell wall proteins, and organization of cytoskeleton.

The specific objectives are to (1) develop quantitative proteomic methods to identify brassinosteroid-regulated proteins, (2) identify microtubule-associated proteins that respond to brassinosteroid treatment; (3) study brassinosteroid regulation of cellulose synthases (CESAs); (4) study brassinosteroid regulation of vesicle trafficking. Brassinosteroid (BR) is a major growth-promoting hormone in plants and is considered a major target for increasing biomass productivity. Brassinosteroid controls many major cellular growth processes including chloroplast development, cell wall synthesis, cytoskeleton organization, and vesicle secretion, which are all critical for biomass accumulation. We have established methods of metabolic labeling of *Arabidopsis* for quantitative mass spectrometry analysis, and have identified a large number of BR-regulated proteins in separate cellular compartments. Our study is generating fundamental knowledge of the molecular mechanisms underlying cellular growth, which is important for improving biomass productivity.

FY 2014 HIGHLIGHTS

Microtubules, assembled from tubulins, are important for many cellular activities, including the movement of cells, cargo vesicles transport, cell morphogenesis, cell wall deposition. We performed proteomic analysis of tubulin/microtubule-associated proteins. To achieve high-confidence quantitation, we used the metabolic ¹⁵N-labelling method in our liquid chromatography tandem mass spectrometry (LC-MS/MS) analysis. After immunoprecipitation of tubulin6-GFP (TUB6-GFP) and GFP proteins from metabolic labeled plants, LC-MS/MS analyses identified over 500 proteins as candidates for tubulin-associated proteins. These include about one hundred proteins annotated with functions related to cytoskeleton. Additional proteins include MAP kinases, calcium dependent protein kinases; several phosphatase, the 14-3-3 proteins, actin, actin depolymerizing factors, lipid transfer proteins, and cellulose synthase family proteins. Some of these proteins potentially regulate microtubule functions. We have performed several BR treatment experiments followed by LC-MS/MS analysis, using ¹⁵N-labeling. We purified phosphopeptides from total protein samples of BR treated and untreated seedlings, and LC-MS/MS analysis identified and quantified 11,047 phosphopeptides on 3,135 proteins. We found phosphorylation decreases at 80 sites and increases at 25 sites on 91 proteins upon BR treatment. These include 7 known proteins of the BR pathway, and the rest unknown previously for a function in BR response. These new BR-responsive phosphoproteins represent new links from BR signaling to various cellular processes, including signaling by other receptor kinases, RNA splicing, translation, and crosstalk with other signaling pathways, as well as cellulose synthesis, cation exchangers, microtubule-associated proteins, and vacuolar protein sorting factor. In summary, our proteomic analyses have identified a large number of proteins with potential functions in steroid regulated cellular growth.

Functional Analysis of Plant Sucrose Transporters

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PROGRAM SCOPE

The goal of this project is to develop a fundamental understanding of the mechanism used by plants transport sucrose. The disaccharide sucrose is the predominant sugar transported in the phloem (vascular tissue) in most plants from photosynthetic leaves to tissues that depend on the import of fixed carbon. Sucrose transporters (SUTs) function in loading sucrose into the phloem in source leaves and in sucrose uptake into cells of sink tissue (such as seeds, roots and other non-photosynthetic tissues). Therefore SUTs function at critical points in the phloem transport pathway. Sucrose transporters are encoded by small gene families in plants and are found in three phylogenetic clades (types). This project has successfully analyzed the transport activity of representatives of each of the three types of sucrose transporters encoded by plants. We can now distinguish each Type by their sequence, activity and subcellular localization. The goal of the project is to study the biochemical transport activities (substrate affinity and specificity, regulation by pH and membrane potential) of SUTs and determine specific amino acid positions in SUTs that control differences in function. During the current DOE-funded project we developed a new assay based on uptake of esculin, a fluorescent substrate, by plant sucrose transporters expressed in yeast. We used a modified gene shuffling technique called Synthetic Template Shuffling (STS) to generate libraries of chimeric sucrose transporters. We expressed these libraries in yeast and selected single yeast cells by fluorescence activated cell sorting (FACS) that were able to transport esculin. In this way we were able to identify five amino acid positions that control the differences in substrate specificity between type I and type II SUTs. This is significant because type I SUTs load the phloem in eudicots while type II SUTs load the phloem in monocots. We used this information to switch the substrate specificity of sugarcane SUT1.

FY 2014 HIGHLIGHTS

We previously identified four amino acid positions that control the difference in substrate specificity between type I and II SUTs (Reinders *et al.*, 2012). We hypothesize that mutagenesis of these positions will produce changes in substrate specificity and/or affinity and will be informative about the function of SUTs. We took advantage of two new approaches we developed during the previous funding period: fluorescent substrate-based transport assay for sucrose transporters (Gora *et al.*, 2012) and selection for single yeast cells expressing active sucrose transporters using FACS (Reinders *et al.*, 2012). We used gene shuffling and mutagenic PCR to generate a library of OsSUT1 mutants that have random codons at the four positions. The library was used to transform yeast which were then treated with esculin and subjected to FACS to select mutant OsSUT1 clones that allow yeast to accumulate esculin. In four rounds of yeast transformations followed by FACS we were able to screen 53,000 library clones and select 16 clones that conferred esculin uptake. The results show that two sequences were isolated. This strategy was successful but was labor intensive. We are going to characterize the two novel clones that were isolated and we may return to this strategy. We are using an additional strategy to first look at each of the four positions with all 20 amino acids substituted. All A86 mutants were functional for sucrose uptake when expressed in yeast. The highest activity was achieved with A86K and lysine is the amino acid conserved at this position in type I SUTs. Solubilization tests were performed with StSUT1-6His and we found that after yeast are lysed, the protein could be efficiently solubilized using 1% Triton X100. The protein was then bound to a Talon NTA column and eluted using imidazole.

Secondary Wall Formation in Fiber Cells

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Funding: \$185,000 (2014)

PROGRAM SCOPE

The objective of this funded project is to carry out biochemical and genetic studies of genes involved in the biosynthesis of xylan, the second most abundant polysaccharide in secondary cell walls. Secondary walls in the form of wood and fibers are the most abundant biomass produced by plants. Understanding how secondary walls are synthesized not only is of importance in basic plant biology but also will potentially provide novel means to modify cell wall composition on the basis of our needs, such as engineering walls more suitable for biofuel production. The goal of this project is to identify and biochemically characterize all the genes involved in xylan biosynthesis. Xylan in dicots is composed of a linear backbone of beta-1,4-linked xylosyl residues, some of which are substituted with glucuronic acid or 4-O-methylglucuronic acid residues and may be acetylated at O-2 and/or O-3. The reducing end of xylan contains a unique tetrasaccharide sequence beta-D-Xylp-(1->3)-alpha-L-Rhap-(1->2)-alpha-D-GalpA-(1->4)-D-Xylp. Xylan from monocots has side chains of arabinosyl residues in addition to glucuronic acid, and the arabinosyl side chains may be cross-linked with each other or with lignin by ferulate. We proposed to genetically and biochemically study genes responsible for xylan substitution and modification. Our proposed work on the study of xylan biosynthesis will not only contribute to our understanding of cell wall biosynthesis in general but also have important economic and agronomic implications, such as providing tools for custom-designing cell wall composition tailored for biofuel production.

FY 2014 HIGHLIGHTS

Xylan, a major polysaccharide in plant lignocellulosic biomass, is acetylated at O-2 and/or O-3 and its acetylation impedes the use of biomass for biofuel production. In *Arabidopsis*, about 60% of xylosyl residues in xylan are acetylated and the biochemical mechanisms controlling xylan acetylation are largely unknown. We have found the essential role of a DUF231 domain-containing protein, ESKIMO1 (ESK1), in xylan acetylation in *Arabidopsis* as the *esk1* mutation caused specific reductions in the degree of xylan 2-O or 3-O-monoacetylation and in the activity of xylan acetyltransferase. Our finding indicates that ESK1 is a putative xylan acetyltransferase required for 2-O- and 3-O-monoacetylation of xylosyl residues in xylan. In *Arabidopsis*, about 10% of xylosyl residues in xylan are substituted with glucuronic acid, of which 60% are methylated at O-4. By contrast, all of the glucuronic acid substituents in *Populus* xylan are methylated at O-4. It is not known how the degree of glucuronic acid methylation in xylan is controlled. We found that simultaneous T-DNA knockout mutations of the three glucuronoxylan methyltransferase genes led to a complete loss of glucuronic acid methylation in xylan in *Arabidopsis* stems. Overexpression of the methyltransferases in wild-type *Arabidopsis* resulted in an up to 5-fold increase in glucuronoxylan methyltransferase activity and as a result, up to 90% of the glucuronic acid side chains in xylan were methylated as opposed to 60% seen in the wild type. Our findings suggest that the degree of glucuronic acid methylation in xylan is largely controlled by the level of methyltransferase activities. We have also performed biochemical characterization of four wood-associated glucuronoxylan methyltransferases in poplar and found that two of them exhibit much higher substrate affinities than *Arabidopsis* ones, which may account for the complete methylation of glucuronic acid residues in poplar xylan.

Cell-Type Specific Hemicellulose Structures in the Root Cell Walls of *Arabidopsis* and *Brachypodium*

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Funding: \$170,000 (2014)

PROGRAM SCOPE

Hemicelluloses comprise a family of abundant polysaccharides in the cell walls of land plants. These include xyloglucan and xylan. The basic structures of these polysaccharides are highly conserved among all land plants, but the more complex structural features vary from plant to plant and from tissue to tissue. This research tests our hypothesis that the structural features of hemicellulosic polysaccharides are tailored to the biological functions of the cell walls into which they are deposited, distinguishing the walls of different cell types and/or cells at different developmental stages. To achieve this end, we use a combination of chemical, enzymatic, immunological and spectroscopic methods to examine the structures of hemicellulosic polysaccharides with high accuracy and sensitivity. For example, we use monoclonal antibodies to implement immunohistological studies that allow us to visualize specific structural variations in different cells. We also perform detailed structural characterization of hemicelluloses extracted from different plants and from mutant plants in which hemicellulose biosynthesis has been impaired. By comparing the immunohistological and chemical analyses for many different cell types, we are able to distinguish species-specific and cell-specific differences in hemicellulose structure. These analyses continue to support our overall hypothesis and provide the fundamental structural information that is required to understand how these polysaccharides function in different cell walls and how the plant modulates these functions by changing specific aspects of hemicellulose biosynthesis.

FY 2014 HIGHLIGHTS

During 2014, we have continued to investigate the biological functions of hemicelluloses by examining differences in root and root hair walls of monocots and dicots and have expanded our efforts to explore differences in the structures of the hemicelluloses in vegetative (flag leaf) and reproductive tissues (tassels) of maize and differences in the structures of the hemicelluloses in selected members of the Lemnaceae. These results have confirmed our previous results that the cell walls of root hairs, which grow by a different mechanism than most plant cells, contain xyloglucan with distinctive structures. We previously discovered that the xyloglucan in *Arabidopsis* root hairs contain an unusual acidic sidechain not found in other tissues of this plant. We have now cloned and expressed the gene encoding the galacturonosyl transferase responsible for attaching the acidic sugar to the sidechain and are in the process of thoroughly characterizing its biochemical and catalytic activity. We also showed that soybean root hairs contain this unusual acidic xyloglucan structure. In addition, we established that xyloglucan with fucose-containing sidechains and a high degree of branching is present in maize cell walls, but only in specific cell types. We obtained convincing new evidence that xyloglucan lacking certain structural features is dysfunctional and can actually harm the plant more than eliminating this polysaccharide altogether. We look forward to performing systematic structure/function analyses that reveal the molecular bases for our observations.

DOE National Laboratories

Metabolic Plasticity, Macromolecular Organization, and Post-translational Regulation of Lignin Biosynthesis

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Funding: \$776,000 (2014)

PROGRAM SCOPE

Phenylpropanoid biosynthesis in plant engenders a myriad of phenolics each with specific biological functions. In particular, as one of the structural components of the cell wall, lignin imparts rigidity and strength to vascular tissues but, meanwhile, it lowers the cell wall's digestibility and negatively affects the conversion efficiency of cellulosic biomass to liquid fuels. The long-term goals of this project are to elucidate the molecular- and biochemical- mechanisms underlying the synthesis and deposition of lignin, and to dissect the concurrent regulatory mechanisms of phenylpropanoid-lignin biosynthesis. Ultimately, we anticipate designing and developing novel biotechnological strategies for improved manipulation of the quantity and structure of lignin in the cell wall. Currently, we have two research objectives: 1) To explore the post-translational regulations and the potential macromolecular organization in phenylpropanoid- lignin biosynthesis, and to define their biological significance; and 2) To evolve monolignol 4-O-methyltransferases to modify the conventional lignin precursors, or to produce novel monomeric precursors, and use these to explore the chemical- and biochemical- mechanisms of lignin polymerization and to modulate lignin content and structure. Previously, we demonstrated that chemically modifying the para-hydroxyl of monolignol via an engineered 4-O-methyltransferase substantially reduced lignin content in the cell wall. We are now developing methods to further tailor its substrate specificity to create a subset of functionally specialized enzymes that are able to discriminate particular monolignols, thereby, to disturb the incorporation of particular lignin precursors into lignin polymer.

FY 2014 HIGHLIGHTS

Phenylalanine ammonia-lyase (PAL) is the first enzyme in the pathway directing carbon flux into the phenylpropanoid branch. By Yeast-Two-Hybrid (Y2H) screening, we identified four *Arabidopsis* Kelch repeat-domain containing F-Box (KFB) proteins that physically interact with PAL isozymes, and mediate PALs' turnover via the ubiquitination-26S proteasome pathway. Manipulating KFB genes' expression reciprocally affects the stability of PAL enzymes and the production and accumulation of phenylpropanoids. Our data suggest that KFB-mediated ubiquitination and degradation of PALs act as a post-translational regulation mechanism, negatively controlling phenylpropanoid metabolism. Using Co-Immunoprecipitation coupled with liquid chromatography-mass spectrometry analysis, and the mating-based split ubiquitin Y2H system, we also explored the potential enzyme complexes associated with the membrane-bound P450 enzymes C₄H, C₃H and F₅H, the hydroxylases involved in lignin biosynthesis. We found that those membrane-bound enzymes strongly and specifically interact with a couple of common scaffold proteins, which result in a unique subcellular localization pattern. Previously, we evolved a set

of monoglignol 4-O-methyltransferases (M4OMTs). To further explore their effects on the energy crop's lignification, we expressed a M4OMT variant in poplar, which results in more than a 50% decrease in S-lignin subunit, along with a considerable increase in condensed cross-linkages, pointing to a substantial alteration in lignin composition and structure in the transgenic poplar. Nevertheless, the saccharification efficiency of wood biomass of the transgenic poplar was increased by up to 62%, compared to the control, suggesting that condensation of lignin is not necessarily correlated with the digestibility of wood biomass in poplar, and that M4OMT-mediated alteration of lignin composition might globally affect the cell wall's structure and the interactions between the cell wall's polymers.

Mass Spectrometric Imaging of Plant Metabolites

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Funding: \$485,000 (2014)

PROGRAM SCOPE

This program is making advances to 1) enhance mass spectrometric imaging (MSI) techniques for determining the distribution of metabolites at very high spatial resolution within plant tissues and cells; and 2) applying these techniques to understand the organization of complex metabolic processes at the levels of single cells and subcellular compartments. Achievements in these interrelated objectives is enabling the unprecedented analysis of genetic stocks that dissect complex metabolic processes and thus bear on the better understanding of biological processes. The application to the plant sciences however, is highly significant to the mission of DOE for the purpose of advanced understanding and thus ultimately the development of technologies for sustainable energy, integrated with food and feed production. This program includes two analytical chemistry groups and a plant metabolic biology group. The team is enabling the integrated development of the imaging technology with its application to the plant sciences, and is thus making significant contributions to the wider plant biology community. This integrated multi-disciplinary team approach is ensuring the development of new technologies to “push” the understanding of complex metabolic processes by enabling the tracking of metabolic intermediates as they move through a distributed metabolic network, and simultaneously become chemically inter-converted. As biological insights are gained via these imaging technologies, are further developing new questions that will “pull” the technology development to enable data acquisition to address specific biological hypotheses. This integrated pull-push strategy that has been developed within this program via the close interactions among the unique team members is further advancing the dissection of plant metabolic biology at high-spatial resolution to levels that are currently unavailable.

FY 2014 HIGHLIGHTS

We made major technological advances that include: 1) ultra-high 5 micron spatial resolution mass spectrometric imaging (MSI) ; 2) enhanced multiplex MSI techniques that increase the speed of data acquisition; 3) development of new matrices for high sensitivity detection of a broader chemical range of plant metabolites; 4) improved sample preparation methods for MSI for analyzing intracellular metabolites; and 5) development of new laser ablation electrospray ionization (LAESI) based MSI using

ultraviolet lasers. These technological advances have been applied to address questions in biological cellular and subcellular imaging of complex metabolic processes, including: 1) C₄ cells of maize leaves; 2) plant-bacterial and plant-insect interactions; 3) specialized metabolism that integrates isoprenoid and polyketide biosynthesis in leaf translucent glands; and 4) cuticle lipid deposition on flower organs.

Quantitative Analysis of Central Metabolism in Seed Storage Synthesis

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Funding: \$679,000 (2014)
PROGRAM SCOPE

Plant biomass is of increasing importance as renewable resources for the production of fuels and of chemical feedstocks that replace petroleum-based materials. Our goal is to increase the basic understanding of the functioning of metabolic processes that define storage metabolism in plants, as a basis for rational engineering of plant storage organs like seeds. By computational modeling of metabolic networks, stable isotope metabolic flux analysis, and biochemical analysis, we study the metabolism of storage synthesis in oil storing seeds. In particular, we study plant species of the cabbage family (oilseed rape, *Brassica napus*, Field Pennycress, *Thlaspi arvense*) that store oil in seeds. Developing embryos are cultured under different light and nutritional conditions. Under each condition, this will provide a detailed view of the particular metabolic state. By comparing the different states, the plasticity of the central metabolism network is revealed. Together, this will increase understanding of the biochemical processes involved in partitioning carbon and nitrogen into seed storage compounds. These studies support the DOE mission to perform fundamental research to lay scientific foundations for new and improved energy technologies. In particular, the analysis and optimization of biochemical pathways relates to fundamental understanding of chemical transformations, photosynthetic energy conversion and energy flow in living systems. This research impacts numerous DOE interests, including improved biochemical pathways for biofuel production.

FY 2014 HIGHLIGHTS

We explored to which extent changes in metabolic flux in central plant metabolism can be inferred by changes in transcripts and metabolites. For this purpose two oilseed rape (*Brassica napus*) accessions which contrast for seed lipid accumulation were compared. On the basis of Metabolic Flux Analysis with *in vitro* culture of immature embryos, the flux distribution in the central metabolism network of both genotypes was determined. In parallel to the flux analysis, metabolite levels of 79 metabolic intermediates within the central metabolism were determined and transcriptome analysis was performed. We found that a large number of genes were differentially transcribed in the two genotypes, including some enzymes/proteins active in major metabolic pathways. However, with a few exceptions, differential activity in the major metabolic pathways was not reflected in contrasting abundances of the relevant transcripts. The conclusion was that transcript abundance on its own cannot be used to infer metabolic activity/fluxes in central plant metabolism. This limitation needs to be borne in mind in evaluating transcriptome data and designing metabolic engineering experiments.

Modification of Plant Lipids

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Funding: \$1,019,000 (2014)

PROGRAM SCOPE

This program is designed to provide fundamental understanding of chemical transformations and energy flow in systems relevant to DOE missions. Specifically to understand the molecular mechanisms involved in the capture of light energy and its conversion into chemical energy through biological pathways. Our overall goal is to create the knowledge needed to improve plant and microbial oils as alternative and improved energy and chemical feedstocks; which will contribute to United States energy and fossil feedstock independence. Lipids and oils are energy-dense compounds that occur in a wide variety of forms, including the storage lipids of higher plants. The molecular mechanisms involved in chiral lipid-modification reactions using fatty acid desaturation as a model are being studied. X-ray crystallography, spectroscopy, molecular genetics, and biochemistry are employed to probe structure-function relationships within these enzymes. Understanding the factors that control the selectivity and specificity of these processes is allowing us to redesign lipid-modification enzymes with improved function. The ultimate goal of this program is to provide the knowledge to enable the optimization of chemical transformations necessary for creating improved plant lipid accumulation in non-food crops.

FY 2014 HIGHLIGHTS

Studies on the oligomerization led to the finding that FAD2 and FAD3 desaturases form hetero-dimers that facilitate metabolic channeling *in vivo*. This finding has implications for the engineering of unusual fatty acid accumulation in crop plants and was published in the Journal of Biological Chemistry. In a follow up study to our work in *Arabidopsis* regarding the engineering of omega 7 fatty acids as renewable chemical feedstocks, we engineered the crop plant camelina to accumulate greater than 70% of omega 7 fatty acids in its seeds. This represents a new source for this feedstock that is an alternative to petrochemicals and was published in the Plant Biotechnology Journal. Collaborative work with BNL PI Changcheng Xu resulted in the elucidation of the triacylglycerol accumulation pathway in *Arabidopsis*. This work resulted in double mutants that accumulated approximately 7% oil in plant leaves. This work, published in The Plant Cell lays the foundation for engineering crop plants to accumulate oil in their leaves as well as in their seeds.

Intracellular Lipid Transfer in the Biosynthesis of Photosynthetic Membranes Lipids and Storage Triacylglycerol

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Funding: \$485,000 (2014)

PROGRAM SCOPE

Intracellular lipid transfer is essential for membrane proliferation, organelle biogenesis and accumulation of storage lipids, but the underlying molecular mechanisms of lipid transfer remain elusive. The overall goal of this project is to understand the molecular mechanisms involved in the biosynthesis and intracellular trafficking of lipids in plants. The specific objectives are to: (1) identify the genes affected in two lipid-trafficking mutants isolated in a forward genetic screen; (2) determine the functional role of the encoded proteins at the molecular, biochemical, and physiological levels; and (3) investigate oil biosynthesis and regulation in vegetative tissues of plants. The results from this study should create the knowledge base to enhance our ability to manipulate the processes that regulate photosynthetic membrane biogenesis and carbon storage in plants, and lay the intellectual foundation for future engineering endeavors aimed at the development of novel biomass crops for the production of nutrition-rich feed and renewable fuels.

FY 2014 HIGHLIGHTS

Two mutant loci were identified through a map-based cloning approach. One encodes a putative membrane protein of unknown function and was designated trigalactosyldiacylglycerol5-1 (*tgd5-1*) because the mutant accumulates trigalactosyldiacylglycerol in leaves similar to previously described four *tgd* mutants. Genetic analysis showed that TGD5 functions in the same lipid trafficking pathway as TGD4. Chloroplast import assays revealed that TGD5 is localized in envelope membranes of the chloroplast. The second mutant locus represents a new allele of *tgd2* mutants. Additional work focused on analyzing the pathway of triacylglycerol (TAG) biosynthesis and its physiological significance in vegetative tissues of plants. We found that phospholipid: diacylglycerol acyltransferase (PDAT) is critical in mediating oil biosynthesis in rapidly growing tissues. Disruption of PDAT1 in the *tgd1-1* mutant background causes serious growth retardation, gametophytic defects and premature cell death in developing leaves. Lipid analysis data indicated that knockout of PDAT1 results in increases in the levels of free fatty acids and diacylglycerol. *in vivo* radiotracer labeling experiments showed that, compared with wild-type, *tgd1-1* exhibits a 3.8-fold higher rate of fatty acid synthesis, which is unaffected by disruption or over-expression of PDAT1. Coexpression of PDAT1 with oleosin boosts leaf TAG content by up to 6.4% of the dry weight without affecting membrane lipid composition and plant growth. PDAT1 overexpression stimulates fatty acid synthesis and increases fatty acid flux toward the prokaryotic glycerolipid pathway. The combined overexpression of PDAT1 with oleosin in *tgd1-1* increases leaf TAG content to 8.6% of the dry weight and total leaf lipid by fourfold. Collectively, these results reveal a dual role for PDAT1 in enhancing fatty acid and TAG synthesis in leaves, thereby protecting against free fatty acid-induced cell death in fast-growing tissues of plants.

Separations and Analysis

Institutions Receiving Grants

Chemical Microscopy of Conjugated Polymers

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Funding: \$420,000 (2014-2017)

PROGRAM SCOPE

Our research is focused on development of new material platforms and analytical spectroscopy methodologies for probing inter- and intra-molecular electronic processes in conjugated nanomaterials. A detailed understanding of the connection between molecular architecture, supramolecular/polymer assembly, and optoelectronic function is critical to the improvement in polymer-based optoelectronics, yet many questions remain outstanding as to how to 'program' specific inter-molecular couplings via molecular structure in order to achieve desired device performance (photostability, charge-separation and charge-transport efficiency). We combine single-molecule spectroscopy tools and new synthetic methodologies to probe intra- and inter-molecular coupling in small-molecule, oligomeric complex structures and crystalline nanoscale supramolecular assemblies in order to understand in detail, the structure-excitonic property relations and elucidate molecular design rules (distances, angles, etc.) for improved performance in organic optoelectronics.

FY 2014 HIGHLIGHTS

The family of rylene dyes is attracting wide research interest as a material platform for small-molecule organic electronics. Recent synthetic work has realized a novel (n-type) small-molecule acceptor, 7,8,15,16-Tetra-aza-terrylene (TAT), single-crystals of which can be grown oriented along the c-axis crystallographic direction for use in organic photovoltaic devices. However, characterization of single TAT crystals reveals highly variable emission spectra and excited state dynamics – properties that strongly influence photovoltaic performance. With our chemical imaging techniques (combined wavelength and time-resolved photoluminescence and resonance Raman imaging) applied to isolated single-crystals, we were able to show that this variability derived from crystal packing defects. This work has recently been published as a cover feature in *PhysChem ChemPhys* (PCCP 16, 15825, 2014) and more recently featured in *Materials Today* (17, 464, 2014). The TAT system also presents an interesting platform for probing directional exciton coupling and charge-separation processes. In a recent collaborative paper published in the *Journal of Physical Chemistry C* ("H-J Aggregate Behavior of Crystalline Tetraazaterrylene: A New Design Paradigm for Organic Materials," 118, 28842, 2014) we showed that crystalline TAT exhibits two distinct coupling mechanisms: A Frenkel (point-dipole) excitonic coupling that is oriented primarily transverse to the crystal growth axis (i.e. along the pi-stacking direction), and a charge-transfer interaction that is oriented primarily parallel to the crystal growth axis. The former gives rise to spectroscopic signatures associated with H-aggregates, while the latter gives rise to J-aggregate behavior. This presents some very exciting opportunities to probe

orientational effects on isolated nanocrystals to, for example, selectively excite charge-transfer states with linearly polarized excitation.

Combinatorial and High Throughput Membrane Synthesis and Testing: Tailoring Membrane Surfaces to Applications

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Funding: \$160,000 (2014-2016)

PROGRAM SCOPE

The goals of our 3-year research program are to expand, refine and optimize the discovery and separation characteristics of new surfaces using the 96-membrane well format with the high throughput-atmospheric pressure plasma (HTP-APP) method and to elucidate the behavior of protein-resistant chemistries. In short, we use combinatorial chemistry to prepare a vastly expanded library of vinyl monomers (AIM 1), graft these newly synthesized monomers, test their efficacy for improving filtration performance, and select winners (AIM 2); fine-tune the grafting and filtration conditions of selected winners (AIM 3), and investigate the underlying mechanistic reasons why the successful monomers are able to perform best (AIM 4). That is, we wish to use combinatorial chemistry to prepare an expanded library of vinyl monomers for APP-grafting of PES UF membranes. Then, use our high throughput 96 membrane-well format to graft, test, and screen for the best performing graft polymerized membranes from Aim 1 using single protein feed filtration. Based on the screening results, we optimize and fine-tune the grafting and filtration conditions of selected winners using our high throughput 96 membrane-well format. Finally, we investigate the underlying mechanistic reasons why the successful monomers are able to perform best. The mechanism can be probed using various different analytical techniques, such as 2D Nuclear Magnetic Resonance (2D NMR), Sum Frequency Generation (SFG), and Mass Spectrometry (MS). We believe that fundamental mechanistic understanding of protein interactions at surfaces and with water will give great insight into the fouling process.

FY 2014 HIGHLIGHTS

Using combinatorial chemistry, a set of diverse monomers were synthesized and tested using our unique high-throughput screening platform to reduce biological fouling on synthetic filtration membranes. To demonstrate its efficacy, the novel monomers were graft-polymerized onto light sensitive poly(ether sulfone) (PES) membranes via Atmosphere Pressure Plasma (APP) polymerization (AIMs 1 & 2). A diverse library was synthesized by reacting a common vinyl ester linker with a library of maleimides containing various different functional groups. This allowed us to produce a library of nine different surfaces and graft them all using the same linker chemistry. Some of the chemistries discovered here are novel R groups (tri-cyclic, ester, azo, and heterocyclic) while others (amide, carboxylic acid, zwitterionic, PEG, and hydroxyl) have been known for some time. This allowed for screening new and interesting monomers and comparing them directly with previously identified “winners”. The modified surfaces were then tested and screened for the best protein-resistant (non-fouling) properties (AIM 3). Membranes, functionalized with carboxylic acid, zwitterionic, and ester groups, had the lowest protein adhesion compared with an unmodified control PES membrane after a static fouling test. After dynamic

fouling, these same functionalities as well as a hydroxyl group exhibited the highest permeability. These monomers performed better than our best previously synthesized amide monomers as well as our best PEG monomers. Hansen solubility parameters qualitatively predicted which monomers performed best indicating favorable interactions with water molecules. Mechanism studies (AIM 4) with SFG and MS were initiated in collaboration with Prof. Poul Petersen, Cornell University, and Prof Daniele Fabris, University at Albany, respectively. Two provisional patents were applied for in 2014: One on chiral surfaces and the other on a new class of synthetic brush membranes.

Molecular Aspects of Transport in Thin Films of Controlled Architecture

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Funding: \$330,000 (2013-2014)

PROGRAM SCOPE

The project has two major objectives. (1) We seek to understand the complex factors that couple reactions to transport when confined in nanoscale architectures. We are developing both single molecule and ensemble measurements to determine the fundamental chemical and physical factors that determine how transport and reactivity are coupled under confinement and crowding in nanocavities, nanopores and nanochannels. We employ single molecule studies of bound redox enzymes and small molecule fluorophores in order to understand redox processes under confined conditions, studying both chemical redox processes catalyzed by oxidoreductase enzymes and electron transfer to small tethered electroactive molecules. In addition, we study electron transfer in nanoscale architectures under conditions designed to alter the fundamental kinetics, e.g. with an added electrocatalyst or in the presence of surface-bound or solution-phase viscosogens. (2) We study reactions in organized geometries that support vectorial transfer of reactants and products in sequential chemical transformations. Quasi-one-dimensional flow in nanopores and nanochannels - characterized by extreme anisotropy between radial and axial transport - presents opportunities to organize coupled reactions for high efficiency chemical transformations. We are studying reactions in special architectures, where chemical reactions are directed to occur at specific locations. This allows us to model and construct high efficiency nano-reactors using electrochemical and photochemical driving forces to generate small molecule reagents at high efficiency in confined geometries. In addition, we utilize both enzymes (oxidoreductases) and inorganic catalysts downstream to carry out high efficiency reactions with the reagents generated *in situ* at the upstream site, thereby leveraging the quasi-1D nature of the flow structure to sequence chemical transformations in space and time.

FY 2014 HIGHLIGHTS

We completed studies of nanopore-mediated redox cycling events and vectorial coupling of transport and electron transfer under both weak-coupling (microchannel) and strong-coupling (nanochannel) conditions. The nanopore-mediated electron transfer studies illustrated the unusual features of chemical reactions carried out in sub-fL volumes, showing, for example, a 100x increase in current at low concentrations when voltammetry is carried out without a background electrolyte, thus implicating electromigration as an effective means of mass transport at the nanoscale. Studies of electron transfer

coupled to electrokinetic flow in the weak coupling conditions that apply in microscale fluidic environments show a split of the applied potential between components that (a) drive fluid motion (iR drop) and (b) drive heterogeneous electron transfer. A model was developed that quantitatively explains the electrochemical behavior under weak coupling. Under the strong coupling conditions that apply in a nanofluidic environment, this is no longer possible, but the shifts in electrochemical waves can still be understood based on the coupling of electric fields generated by the external (field-inducing) electrode and the working electrode. These studies together illuminate the special character of electron transfer reactions carried out in nanometer-scale structures where the physical scaling lengths characteristic of electrified fluids, e.g. Debye length, are commensurate with the size of the structure.

Targeting DOE-Relevant Ions with Supramolecular Strategies

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Funding: \$160,000 (2014)

PROGRAM SCOPE

The effectiveness of three popular strategies for supramolecular anion recognition is being evaluated and compared targeting ions important to the DOE mission, particularly tetrahedral ions such as sulfate and perrhenate. The goal of the first objective is to assess the influence of secondary, tertiary and quaternized amines as well as macrocyclic size on anion binding using mixed amine/amide macrocyclic hosts. Competitive binding studies are focusing on ions of differing charges: perrhenate (-1) as a surrogate for pertechnetate, sulfate (-2), and phosphate (-3). These ions are problematic in tank remediation (Low Activity Wastes, High Level Wastes, and in tank run-off). The goal of another objective is to synthesize connected molecular organic frameworks (MOFs) to leverage and expand the anion binding capabilities of the hosts. Ag(I) (noted for its linear coordination propensity) is being used for one-dimensional MOFs, and Pd(II) and Pt(II) for square arrays. A new “duplex” Pd(II) connector is also being explored for additional linear MOF linkages. Pyridine groups appended to the macrocycles are being used to link the hosts through metal ion coordination. The goal of a third objective is to explore tricyclic molecules with both anion and cation binding sites as ion pair hosts. The targeted cation in these studies is cesium ion, due to the relevance of cesium-137 in nuclear waste remediation.

FY 2014 HIGHLIGHTS

During the past year, we made considerable progress on refining synthetic strategies for hosts and on the development of novel extended molecular frameworks based on macrocyclic anion hosts. In the area of synthetic strategies, we are now able to isolate significant quantities of 3+3 and 4+4 condensates of diethylene triamine or dipropylene triamine with 2,6-disubstituted pyridines. These expanded macrocycles could potentially bind multiple anions/cations. We also found that mixed amide/amine macrocycles that possess at least one secondary amine readily react with carbon dioxide in the atmosphere, forming 1:1 (in the 2+2 macrocyclic condensate) and 1+2 (in the 4+4 macrocyclic condensate) macrocycle:carbon dioxide adducts. The resulting carbamates are stabilized by intramolecular hydrogen bonding, but carbon dioxide is released on heating. This chemistry is being explored further. Exciting progress has been made in the synthesis of extended macrocyclic molecular

frameworks. We have successfully attached pyridine side-chains to the 2+2 macrocycles, resulting in two arms for linking macrocycles through metal ion coordination. We have also isolated and crystallographically characterized a Ag(I)-connected extended framework in the 2+2 adduct and a single macrocyclic unit with Pd(II) pincer complexes attached to the two pendant pyridines. While binding studies indicate that the new complexes bind anions, we have no structural specifics as to mode of binding to date. To extend the dimensionality of the pincer-containing macrocycles, we synthesized and crystallographically characterized what we believe is the first example of a di-Pd(II) “duplex” pincer complex with a 2,3,5,6-tetraamido-substituted pyrazine. A porous gelatin-like salmon-colored product is obtained when the di-Pd(II) duplex is reacted with the pyridine-appended 2+2 macrocycle. The physical and chemical properties of this jello-like product are currently under investigation.

Electrically Driven Ion Separations in Permeable Membranes

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Funding: \$160,000 (2014)

PROGRAM SCOPE

This project explores whether applied electrical potentials can greatly enhance rejections and selectivities in energy-efficient, membrane-based ion separations. Thus, one facet of the research includes synthesis of dense membranes with conductive skins to enable application of electrical potential drops at the membrane surface. Positive membrane potentials with respect to the feed solution should lead to exclusion of cations and provide selectivity between cations with differing charge. At sufficiently high potentials, exclusion of cations may lead to complete salt rejection, which is potentially valuable for desalination. However, the effects of applied potential are greatest at low ionic strength. Thus, the combination of applied potentials and a membrane skin that dissolves only a low concentration of ions may prove especially powerful. A second area of the research applies potentials across porous membranes to investigate whether countercurrent electrophoresis can separate ions in membranes with high throughput. In these separations, convective flow forces ions through the membrane, whereas electromigration moves ions in the opposite direction. This leads to extensive rejection of ions with high electrophoretic mobilities and less rejection of ions with lower mobilities to give high selectivities. However, challenges in these separations include concentration polarization at the membrane-feed interface and inhomogeneous flow. Current research aims to overcome these challenges. The final area of this research examines electrodialysis through remarkably selective polyelectrolyte multilayer films on ion-exchange membranes. Electrically driven transport yields much higher selectivities than flow through membranes because significant flow occurs through membrane defects. Studies of selectivity as a function of ion concentration and current density are elucidating the effects of concentration polarization and ion adsorption on these separations.

FY 2014 HIGHLIGHTS

Electrodialysis membranes typically exhibit modest selectivities between monovalent and divalent ions. In contrast, this research shows dramatic enhancement of the monovalent/divalent cation selectivities of ion-exchange membranes through coating with multilayer polyelectrolyte films. Remarkably, even

with overlimiting currents, K^+/Mg^{2+} electro dialysis selectivities reach values >1000 , and similar monovalent/divalent cation selectivities occur with feed solutions containing K^+ and Ca^{2+} . For comparison, the corresponding K^+/Mg^{2+} selectivity of the uncoated membrane is only 1.7. When the source phase contains high salt concentrations (0.1 M KNO_3 and 0.1 M $Mg(NO_3)_2$), K^+ carries essentially all the current, and the K^+/Mg^{2+} selectivity is $>20,000$, presumably because the applied current drops below the diffusion-limited value for K^+ . The high selectivities of these membranes may enable electro dialysis applications such as purification of salts that contain divalent or trivalent ions. Studies of countercurrent electrophoresis show that applied potentials lead to selective rejection of K^+ compared to Li^+ . However, concentration polarization limits both rejection and selectivity in this system, so future work will examine new cross-flow geometries. Other research highlights include development of methods to coat membranes with a thin, conducting Au layer to apply electrical potentials at the membrane surface. The coating procedure includes formation of Au nanoparticles and subsequent electroless deposition.

Preparation of Chemically Functionalized Surfaces through Ion Soft Landing and Ion/surface Reactions under Vacuum and in the Ambient Environment

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Funding: \$330,000 (2013-2014)

PROGRAM SCOPE

This project seeks to explore the capabilities of gas-phase ions as reagents to modify surfaces. The method of interest is ion soft landing (SL), where low energy atomic and polyatomic ions are deposited onto surfaces. Traditionally, SL experiments are performed under vacuum where there is exact control of the chemical nature of the reagent, but limitation in the number of ions available for surface modification (low current). To circumvent this, our lab has demonstrated the ability to modify surfaces in the ambient environment, where higher currents are possible at the cost of complete control of the chemical nature of the reagent ions. With these abilities, we began to seek methods to produce surfaces of highly desirable chemical properties, including catalytic properties. New ionization methods are being developed which produce both atomically precise and larger nanoparticles. The properties of the nanomaterials are being investigated for uses in catalysis, surface enhanced Raman spectroscopy, and electrochemistry. Collaborations with PIs T. Pradeep (IITM, India) and Libor Kovarik (PNNL, WA) are carried out to expand the applicability of ion deposition modified surfaces.

FY 2014 HIGHLIGHTS

Ambient ionization and deposition of noble metals (Au, Ag, Cu, Pd) has been developed to synthesize nanomaterials for heterogeneous catalysis. Electrolytic spray ionizes bulk noble metals directly to atomic dispersion in the charged spray plume. Depositing this plume creates noble metal clusters and nanoparticles without capping agents, which is ideal for heterogeneous catalysis. A heterogeneous redox catalysis reaction was carried out in solution phase, the result of which indicated that the catalyst prepared in this way is extremely active and efficient. Adding ligands to the electrolytic spray solution, organometallic catalyst was synthesized and used for polymerization reactions. Besides individual

nanoparticles for heterogeneous catalysis, ambient noble metal ion beams have been used to modify surfaces to create functional materials. Depositing noble metal ion plumes onto various surfaces, composite nanostructures have been created *in situ*. Nanostructured surface patterns have been created by electrostatically manipulating the ion plume. The modified surfaces were functionalized using only nanograms of noble metal. Surface enhanced Raman spectroscopy (SERS) has been carried out to demonstrate the rapid surface modification for optical sensing applications. Another new ionization source for production of atomically precise metal clusters based on electrospray ionization was developed. Metal salts of interest are electrosprayed, passed through a heated loop, and undergo harsh collisions, allowing for the decomposition of the metal salt to produce atomically precise metal clusters. This ion source has been used to generate cluster cations and anions of silver, palladium, and bimetallic palladium-silver. These ions have been reacted in the open air with various reagents to study their initial reactivity, and study of their reactivity under vacuum is underway for industrially important reactions such as propylene epoxidation.

Fluoropolymers, Electrolytes, Composites and Electrodes

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Funding: \$175,000 (2014)

PROGRAM SCOPE

New fluoroionomer electrolytes and fluoroionomer / carbon nanocomposite electrodes suitable for use in fuel cells, batteries and other electrochemical devices (e.g. water desalination, electrodialysis, flow batteries) are being created and their properties examined. Work is pursued in three principal areas; (1) new fluorinated monomers and ionomers; (2) membrane separators made from new ionomers; and (3) catalytic electrodes made from fluorinated ionomers combined with nanoporous carbon electrocatalyst supports. The research exploits a unique capability at Clemson University for the safe handling of large amounts (kilogram quantities) of tetrafluoroethylene (TFE) gas, as is needed to make experimental quantities of new TFE-based fluoropolymer ionomers. New ionomers and ionomer / carbon nanocomposite electrodes are created with the aim of simultaneously increasing transport rates for electrons and ions, and fuels, oxidants and water, throughout the full three-dimensional structure in fuel-cell and battery electrodes and membrane separators. The combination of high-activity electrodes with high-conductivity fluoropolymer ionomers having very good chemical and thermal stability will provide a route to devices having high activity and long service life.

FY 2014 HIGHLIGHTS

Tetrafluoroethylene (TFE) is normally a highly explosive gas but we have found that when mixed with CO₂ it may be rendered completely safe. Fundamental studies on the relative reactivity of various trifluorovinylether (TFVE) monomers with TFE were pursued with the aim of understanding how to combine monomers to achieve specific ion-exchange capacities in ionomers. New TFVE monomers containing organocation groups as hydroxide salts were studied with the aim of preparing alkaline fluoropolymer ionomers suitable for use in alkaline exchange membrane (AEM) fuel cells. Alkaline fuel

cells offer the prospect of electrochemical energy conversion with a dramatically diminished need for platinum-group-metal catalysts, but they have not yet been widely developed due principally to limitations on the alkaline stability of ionomers. We hope to create new ionomers having high ionic conductivity with much improved alkaline stability. We also studied the properties of mixed ionic / electronic conductive (MIEC) electrodes. We reported a means for independently measuring electronic and ionic contributions to electrical conductivity and are using that method to study new electrodes made from mesoporous carbon supports in which fluoroionomer electrolytes are covalently bound to the interior of the support pores. These studies will reveal the degree to which ionomer electrolytes can facilitate ion transport inside the pores of mesoporous materials, as is needed to achieve high activity. We also reported on the oxygen reduction reaction (ORR) activity of platinum catalyst on supports that had been modified by covalent attachment of fluoropolymer electrolyte. Specific ORR activity was increased by approximately 20% for supports having bound electrolyte relative to those that did not.

Separations and Analysis using Bipolar Electrodes

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

Our objective during the current project period was to further understand and expand bipolar electrodes (BPEs) employed for: (1) the efficient evaluation of large arrays of electrochemical catalysts and (2) to perform continuous ion separations. BPEs do not require a direct electrical connection because they can be powered by an externally applied potential bias. Therefore, BPEs lend themselves to the rapid parallel analysis of dense microscale arrays of electrochemical catalyst candidates where making direct electrical measurements is difficult and serial readout slows throughput. With regard to our separations work, we have combined our experiments with numerical simulations carried out by our collaborator, Prof. Ulrich Tallerek (Philipps-Universität Marburg, Germany). These simulations have supplemented our experiments to provide an increased understanding of the underlying physical phenomena driving BPE driven ion separations.

FY 2014 HIGHLIGHTS

Bipolar electrodes (BPEs) provide a powerful and convenient means for evaluating electrocatalyst candidate materials in parallel for electrochemical reactions related to energy applications. BPEs used for screening experiments rely on the fact that the two types of electrochemical reactions, oxidations and reductions, must occur at the same rate because of electroneutrality. This means that an oxidation reaction (for example) can report on the progress of an electrocatalytic reduction reaction. The main advantage of BPEs for screening is that large arrays of electrodes can be operated and monitored in parallel using simple instrumentation: a DC power supply and an optical microscope. Our approach for screening electrocatalysts using BPEs is simple: candidate catalyst materials are dispensed onto the cathodic poles of individual BPEs, the arrays are placed inside a bipolar electrochemical cell consisting of a confined fluidic space and a pair of driving electrodes, the fluidic space is filled with electrolyte solution, and then a voltage is applied between the two driving electrodes. This results in the reductive

screening reaction being driven at the same time and same rate as a reporting oxidation reaction, such as the electrodisolution of a thin metal film. During this project period we used BPEs to screen 11 distinct compositions of each of three bimetallic electrocatalysts and tested their effectiveness for the oxygen reduction reaction (ORR). The Pd-Co electrocatalysts proved to be more effective than the Pd-Au or Pd-W bimetallic analogs. However, we showed that interpretation of the results of studies such as this requires caution due to catalyst instability and differences in the morphologies of the catalysts that depend on the relative amounts of the two metals present.

Self-Assembled Ionophores: Continuing in New Directions

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PROGRAM SCOPE

Overall research goals: Our goal is to build “self-assembled” ionophores that selectively bind and transport ions. We have used non-covalent interactions to synthesize such receptors. For example, lipophilic guanosine nucleosides hydrogen bond to give G-quadruplexes that selectively bind and transport cations. We have also developed a series of anion transporters based on molecular self-assembly strategies. Our goals include: 1) learning how to control structure & dynamics of self-association and ion binding; 2) design self-assembled ionophores that selectively bind various ions and 3) construct supramolecular structures that function as synthetic ion channels.

FY 2014 HIGHLIGHTS

Supramolecular Assemblies that Form Robust and Functional Hydrogels. We recently published a communication in the Journal of the American Chemical Society (DOI: 10.1021/ja507506c) that described an extraordinarily stable and functional hydrogel made from guanosine and potassium borate. We took advantage of the self-assembly of guanosine to make supramolecular hydrogels for use in drug delivery, cell culture, and tissue engineering. The hydrogel remains intact for over a year in salt water. The hydrogel assembles into G·K⁺ quartets. Borate ions enhance its self-assembly by reacting with guanosine, we found by examining the hydrogel with cryogenic transmission electron microscopy, circular dichroism, and solid-state NMR spectroscopy. We introduced cationic dyes, as well as other nucleosides, into the gel. The gel's stability and adaptability to these additions suggest that it could be developed for a variety of clinical and research applications, including metal ion separations.

New Cl⁻ Anion Receptors/Membrane Transporters. We extended our use of self-assembly to prepare compounds that transport Cl⁻ and HCO₃⁻ anions across bilayer membranes. Using liposomes we compared the H⁺/Cl⁻ co-transport activity and the Cl⁻/HCO₃⁻ anion exchange properties of a series of synthetic molecules and natural products, the prodigiosins. These compounds' ability to transport Cl⁻ and HCO₃⁻ at micromolar concentrations, their low molecular weight and simple preparation make them lead platforms for building new approaches toward selective ion separations.

Optical Mass Spectrometer and Photoacoustics

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PROGRAM SCOPE

Experiments are being carried out to determine the characteristics and sensitivity of a photoacoustic pyrometer. The device is based on a photoacoustic cell equipped with two entrance windows to a single chamber, which, when irradiated by two different sources with different radiances, an acoustic signal is generated. When calibrated, the pyrometer has the capability to determine temperature differences. The salient characteristic of the pyrometer is that a null can be determined with high precision as a result of the remarkable sensitivity of the photoacoustic effect. To date, experiments have shown a sensitivity of tens of mK for the temperature difference between two black radiators. A theory for the motion of a sphere in an intensity modulated, focused light beam has been formulated. It has been shown that the motion of the levitated object obeys an inhomogeneous Mathieu equation. As such, there are regions of stable, oscillatory motion and other regions where the amplitude of motion is large. By varying the modulation frequency, it has been shown that the ratio of the optical force to the gravitational force can be determined. When an additional force from, for instance, gas flow is included, the mathematics show that it is possible to determine the mass of the particle. Experiments are proceeding to realize a device capable of measuring radiation forces and masses of levitated objects. In another project, the mathematics for a photoacoustic effect excited by continuous radiation have been developed to show that spontaneous oscillation of an absorbing gas in a resonator is possible. The principle of the effect is based on the fact that a photoacoustic increase in pressure at an antinode of a resonator is accompanied by an increase in absorption. Research is being carried out to determine if the effect can be generated with a carbon dioxide laser.

FY 2014 HIGHLIGHTS

Experiments have shown the feasibility of using a special photoacoustic cell that alternately views two surfaces through two optical chopping wheels as an infrared "optical" pyrometer. The device generates a signal proportional to the difference in the infrared radiation flux from the two bodies. An important feature of the pyrometer is that it is based on the photoacoustic effect, which is known to have high sensitivity to weak absorptions. As a consequence, the pyrometer becomes a highly sensitive null detector so that the radiance of one object can be compared with that of a standard. Experiments have shown that the device can detect temperature differences of 49 mK for two blackened surfaces. When a short pulse laser irradiates an optically absorbing surface in a transparent fluid, enormous thermal gradients are produced between the surface and the fluid. For instance, for a 1 J, 10 ns laser beam directed at an absorbing water layer having an absorption coefficient of 0.1 cm^{-1} , temperature gradients on the order of 105 K m^{-1} are generated. A theory showing the effects of large thermal gradients on photoacoustic waveforms has been completed based on a new wave equation derived from the coupled differential equations that describe the photoacoustic effect. The wave equation predicts high frequency pressure transients caused by rapid heat flow generated as a consequence of the laser-induced thermal

gradients. In experiments using a 10 ns, 532 nm beam from an Nd:YAG laser used to irradiate weakly absorbing bodies and thin films, the waveforms predicted by theory have been shown to exist.

Binding Anions Selectively with Modular Triazolophanes and Releasing Them with Light

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Funding: \$140,000 (2014)

PROGRAM SCOPE

The goals of this project are to (Aim 1) investigate the fundamental properties of shape-persistent receptors for selectively recognizing polyatomic large anions, and, (Aim 2) to regulate anion concentrations using light-active receptors. This knowledge should provide practitioners with greater guidance during the design of receptors for specific goals: e.g., in the light-gated extraction of specific anionic salts of radionuclides for the management of waste in the nuclear fuel cycle.

FY 2014 HIGHLIGHTS

Towards Aim 1, we have been investigating how to design receptors for polyatomic anions with potential for use in the nuclear fuel cycle. To this end, we examined bifluoride recognition, a linear triatomic anion, F-H-F. Initial computations indicated bifluoride and chloride to have similar binding to the triazolophanes in gas phase. However, solution studies showed they were different. Computations suggested a tilting of the bifluoride could account for the difference. Structural variations to the triazolophane were screened using density functional theory yielding a design that eliminated tilting. Correspondingly, the bifluoride binding affinity was now found to match chloride. Our findings demonstrate the promising ability of computer-aided design to fine-tune the match between receptors and a desired anion. (J. Am. Chem. Soc. 2014, 136, 5078) We have encountered a challenge in describing polyatomic anions because their charges are situated on multiple sites thus creating issues with the design of receptors. We have started to address this challenge using cyanide as a model anion. We used three approaches to show the N end of cyanide forms slightly better hydrogen bonds even though it is not the site of protonation or covalent bond formation. (J. Phys. Chem. A 2014, 118, 7418)

Towards Aim 2, aryltriazole-based foldamers have been created to catch and release Cl anions upon light irradiation of end-appended azobenzenes. A hydrogen-bonding array interlocks the ends of the foldamer together with its helical core. This hydrogen-bonding array has a greater influence on stabilizing the helix than the π -stacked seam. Thus, we show how to enhance the difference between Cl binding and release using light-dependent control over the foldamer's helix stabilization. We achieved a 10-fold improvement over our first design. (J. Org. Chem. 2014, 79, 8383)

Fundamental Structure/Property Studies of Gas Separation Membrane Polymers

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Funding: \$155,000 (2014)

PROGRAM SCOPE

The overarching goal of this fundamental, experimental research program is to systematically synthesize, characterize, and, ultimately, rationally tailor a novel class of polymeric membrane materials with the chemical and thermal stability as well as separation properties required for gas separation applications. This program has exploited and further developed our discovery (Science 318, 254 (2007)) that polymers prepared by thermal rearrangement of soluble aromatic polyimides containing ortho-positioned functional groups, such as OH, exhibit unusually high gas permeability and selectivity values. Furthermore, early studies of this class of materials suggest that they are very robust chemically (i.e., insoluble in all known solvents) and resistant to plasticization.

FY 2014 HIGHLIGHTS

There has been a worldwide debate in the literature regarding the exact chemical structure of thermally rearranged (TR) polymers, and we made what we believe is a definitive contribution to unambiguously answer this question, at least for one of the most promising TR polymers (Polymer 55, 6649 (2014)). We also published an extensive review article on polymeric gas separation membranes in August 2013 (Polymer 54, 4729 (2013)); it has been cited 54 times and was one of the most downloaded articles in Polymer for much of 2014. We have worked closely with a major industrial gas separation company to reduce TR polymers to commercial practice. These polymers are scheduled to begin to be used shortly in On-Board Inert Gas Generation Systems (OBIGGS) aboard commercial aircraft to blanket fuel tanks with nitrogen-rich gas to reduce fire hazards.

EARLY CAREER: Design Synthesis and Characterization of Triptycene-Containing Macromolecules with Hierarchically Controlled Architectures as Functional Membrane Mate

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Funding: \$195,000 (2014)

PROGRAM SCOPE

The overarching goal of this project is to develop advanced triptycene-containing polymer membranes with hierarchically controlled architecture and morphology over multiple length scales for important energy intensive separations and clean energy production. The key thrusts of the work are: 1) macromolecular design, synthesis and characterization of a new series of triptycene-containing polymers with systematically varied structures, and 2) determination and analysis on membrane transport properties caused by the structure variations. A diverse but systematic set of triptycene-based diamine monomers will be synthesized for polyimides synthesis, which will allow us to explore effects of substituent groups, linkage geometry, chain rigidity, macromolecular packing on free volume architecture and consequent final membrane transport properties. We will evaluate fundamental transport parameters (diffusivity and solubility) to understand thermodynamic vs. kinetic factors

contributing to separation performance. A special focus will be upon the correlation between free volume architecture (size and size distribution) induced by triptycene-monomer structure variations and membrane properties. The knowledge obtained will aid in predictably creating highly controlled yet tunable macromolecular architectures and morphologies enabling highly efficient membrane separation technologies.

FY 2014 HIGHLIGHTS

A major development that has come out of the studies during this past contract period has been the discovery that free volume architecture (size and size distribution) in the triptycene-containing polyimides can be feasibly tuned via alteration of the substituent groups neighboring the triptycene moiety along the polymer backbone. This finding provides a new dimension in finely tuning the membrane transport properties via rational macromolecular design using triptycene, or more generally, triptycene unit. Specifically, we have successfully synthesized a first set of key monomers, i.e., triptycene-1,4-diamines, along with the corresponding new polyimides. The obtained robust membranes are both highly permeable and highly selective. We are in the process of sorption tests to evaluate respectively kinetic (diffusivity) and thermodynamic (solubility) contributions to separation. We continue to pursue a second set of specialty monomers, i.e. triptycene-2,6-diamines, which has proven much more difficult to synthesize. We have also started the synthesis of dually-selective membranes by incorporating CO₂-philic PEO segments into triptycene-based polyimides and are in the process of polymer synthesis and film casting and tests.

Analytical Spectroscopy Methods for Liquid/Solid Interfaces

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

Liquid/solid interfaces play a key role in numerous aspects of energy-related chemistry. Many steps in chemical analysis (separation, preconcentration, selective detection) involve adsorption or binding of target species to chemically-modified solid surfaces in contact with liquids. Applications of liquid/solid interface chemistry including catalysis, adsorption or selective binding of molecules or metal ions, chromatographic separations, and environmental remediation, generally employ porous support materials for immobilizing ligands or catalytic sites. The high specific surface area of porous particulate materials (porous oxides or polymers) provides large capacities for adsorption, binding, or catalysis. The challenge for spectroscopic investigation of porous materials is that nearly all of their surface area resides within the porous structure; thus relevant methods to investigate these materials must be capable of interrogating chemistry inside the porous structure. Porous solid surfaces often exhibit heterogeneity in structure and reactivity; thus spectroscopic imaging methods within the porous material are needed to characterize spatial distributions of chemical structure and interfacial interactions. To address these measurement challenges, the scope of this research program is to develop spectroscopic imaging methods for analysis of chemical processes within porous particles. Specifically, we employ confocal Raman microscopy to determine the chemical composition and

structure of interfacial species within individual porous particles. The kinetics of molecular transport within porous particles are being characterized by intraparticle single-molecule fluorescence imaging, to understand their impact on the efficiency of chemical separations and on the time response of separations and sensors.

FY 2014 HIGHLIGHTS

Extraction of PAH compounds into small (sub-pL) volumes was accomplished by using a single chromatographic particle as a collector and Raman microscopy for in-situ detection. By comparing Raman scattering intensity of the analyte to that of the C₁₈-chains in the particle, it is possible to quantify the extracted compound within the particle. The gain in concentration for pyrene was a large factor, 48,000, allowing this PAH compound to be detected from a 10-nM solution. The method requires only selective accumulation of molecules into a high surface-area porous particle, which provides Raman microscopy with nanomolar detection capabilities. Small polymeric particles are increasingly employed as adsorbent materials, as molecular carriers, and in preconcentration applications. The Harris group employed Raman microscopy to investigate the synthesis, structure, and application of individual porous polymeric surfactant particles produced by polymerization of sodium 11-acrylamido-undecanoate. These particles contain hydrophobic domains that can be used to accumulate molecules for adsorption applications, which was also evaluated by Raman microscopy. To investigate the dynamics of molecular transport within porous particles, imaging-fluorescence-correlation spectroscopy was adapted to measure diffusion of small numbers of fluorescent molecules within chromatographic silica particles, to compare with their diffusion at a planar surface. The results show that diffusion on a planar substrate is much faster than diffusion through the particle. By accounting for the greater surface area that a molecule must explore to diffuse macroscopic distances through a nanoporous particle, the molecular-scale diffusion rates on the two surfaces could be compared and were found to be equivalent. These results provide support for the relevance of surface-diffusion measurements on model planar surfaces to the dynamics of molecules on the internal surfaces of porous particles.

Elucidation and Reduction of Interference Effects in Inductively Coupled Plasma Spectrometry

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PROGRAM SCOPE

Rare-gas plasmas are among the most useful tools of analytical chemistry. They take several forms, from the ICP used for atomic emission and mass spectrometry to the DART (Direct Analysis in Real Time) employed in ADI-MS. Plasmas provide exceptional sensitivity, flexibility, and selectivity. Unfortunately, their performance for quantitative analysis often falls short of what is needed. Of necessity, plasma-based methods are relative; that is, they rely on standards to calibrate an instrument. As a result, any difference in response between those standards and the species to be determined (the "analytes"²) causes an error, and yields values that might be either higher or lower than the true value. Such errors can arise from many sources, but the root problem arises because the overall composition of a sample (the sample 'matrix') influences the analyte signal. We believe the most promising path for overcoming

matrix interferences is by a thorough fundamental understanding of what causes them. From this understanding, it might then be possible intelligently to select sample additives, to modify the atomic or ion source, or to alter operating conditions in a way that alleviates or eliminates the interferences. Alternatively, if enough is understood about the source, the emission or mass spectrometer, or the interferences themselves, it might be possible to devise monitoring and diagnostic strategies that can detect the presence of an interference and modify the instrument operation in a way that minimizes it. Failing this capability, such strategies should at least be able to flag a sample in which an interference is sensed. It is the goal of the proposed studies to provide such fundamental knowledge and to devise appropriate diagnostic approaches.

FY 2014 HIGHLIGHTS

Because our DOE-funded program has several facets, progress in each facet will be briefly highlighted here.

- Detecting and correcting matrix interferences in ICP emission spectrometry: We have devised a new strategy for detecting matrix interferences when an ICP is viewed in an end-on fashion and fed with a sample in an organic solvent. The method is based on the fact that the ratio of chosen spectral lines changes in the presence of an interference when the sample solution is diluted. The same gradient dilution apparatus can then be used to calibrate the instrument.
- Ambient desorption/ionization mass spectrometry with a flowing afterglow source (FAPA): We have characterized the interaction of the FAPA plume with a sample surface by means of schlieren imaging. The same method allows us to optimize fundamentally the sampling of the resulting material into a mass-spectrometer interface. In addition, we have determined the effect of ambient conditions (temperature, humidity) on the resulting mass spectra. A new FAPA design, based on a microwave discharge, has also been evaluated, and the FAPA used to detect counterfeit electronic components.
- Distance-of-flight mass spectrometry (DOFMS): We have coupled an inductively coupled plasma ion source to our DOFMS and used it with a laser-ablation system for sample introduction. Despite the fact that an inexpensive spatially selective detector (microchannel plate + phosphor screen) was being used, the detection limits, isotope-ratio precision, and precision rivaled that of far more costly and less versatile instruments. In addition, we showed that use of constant-momentum acceleration (CMA) in time-of-flight mass spectrometry (TOFMS) yields improved resolution over conventional constant-energy acceleration. This realization allows TOFMS to be used in two alternating modes: conventional and CMA, with the former providing broad mass coverage and the latter enhanced resolution over a narrower mass range.

Coordination Chemistry Derived Materials Featuring Nanoscale Porosity and Selective Chemical Separation

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

The project research objectives are to design, understand, and utilize new materials having nanoscale porosity – specifically, new metal-organic frameworks (MOFs) – to achieve energy-efficient separations of technologically relevant or DOE-mission-relevant chemical mixtures, especially mixtures of gases and/or vapors. Achieving these objectives has entailed the development of new tools for computational modeling and new methods for synthesizing MOFs, especially MOFs that are difficult or impossible to access via conventional methods.

FY 2014 HIGHLIGHTS

Although an enormous variety of MOF compounds has been reported, many MOFs that could be highly effective as selective sorbents appear impossible to access via conventional synthesis methods. With this problem in mind, we have focused on three new or emerging MOF synthesis strategies, AIM, SALE, and SALI. AIM (Atomic-Layer-Deposition In MOFs) is an example of a broader set of approaches that can be classified as post-synthesis modification. SALE and SALI (solvent-assisted-ligand-incorporation) are examples of a set of synthesis approaches that can be viewed as building-block-replacement approaches. AIM: This new synthesis technique provides a way of creating uniform arrays of metal-oxide, mixed-metal-oxide, and metal-sulfide clusters. Our intent is to use these clusters to accomplish selective binding and separation of mixtures of small molecules. We have recently demonstrated the experimental feasibility of AIM with the platform MOF, NU-1000. SALE: In several recent reports we have shown that otherwise synthetically inaccessible MOF materials can be accessed by first building structural analogues and then subjecting the materials to solvent-assisted-linker-exchange (SALE). We are just beginning to explore the implications of SALE for synthesis of new materials for chemical separations. SALI: Closely related to SALE (i.e. exchange of structural ligands) is solvent-assisted incorporation of desired nonstructural ligands. Using the platform MOF, NU-1000, as a test case, we have found that a wide variety of pore-modifying ligands can be controllably installed, including ligands whose incorporation via direct synthesis methods is not possible. Examples include pendant-catechols (metal-ion binding sites), organic acids, organic bases, thiols, fluorocarbons, “click”-susceptible azide or acetylide functionalities, amino acids, and oligopeptides. Our intent is to systematically alter the affinity of MOF channels for selected molecular components of chemical mixtures.

Molecular-Level Investigation of Diffusion Behaviors within Cylindrical Nanoscale Pores

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PROGRAM SCOPE

The goal of this project is to develop a quantitative molecular-level understanding of mass transport mechanisms within solution-filled nanoporous media. Cylindrical nanopores having well-defined sizes and surface properties are obtained from self-organized materials such as surfactant-templated mesoporous silica (STMS) and cylinder-forming block copolymers (CFBCP), and are employed as model systems. Mass transport is investigated using single-molecule fluorescence techniques including single

molecule tracking (SMT) and fluorescence correlation spectroscopy (FCS) as well as ensemble techniques such as fluorescence recovery after photobleaching (FRAP). These two types of methods are used to measure identical materials for directly comparing between single-molecule and ensemble behavior. The direct comparison is expected to reveal key molecular-level processes governing the rate and selectivity of molecular permeation through nanoporous media employed in chemical separations and catalysis, and as membrane separators in fuel cells and batteries. The comprehensive understanding that will result from these studies will facilitate the engineering of nanoporous media optimized for energy-related applications. In addition, we are pursuing new experimental approaches as means to overcome certain fundamental limitations of existing fluorescence techniques used for mass transport measurements. Previously, we developed a simple, quantitative method (orthogonal regression analysis) to quantify the orientation and order of nanopores by tracking the one-dimensional motions exhibited by single molecules diffusing within them. We applied it for assessing microscale domains with differently oriented nanopores in STMS films and also for revealing flow-induced alignment and diffusion pathways in rod-shaped block copolymer micelles. We have also developed a new polarization-dependent SMT method to quantify the wobbling motions of single molecules confined within nanoscale pores.

FY 2014 HIGHLIGHTS

During FY2014, we investigated elongation, alignment and guided electrophoretic migration of individual fluorescently-labeled double-stranded DNA molecules within flow-aligned surfactant mesophases (H. Xu, *et al.*, J. Phys. Chem. B 2014, 118, 4151.). This work demonstrated that the DNA molecules could be elongated parallel to the cylindrical micelles comprising the (near-surface) mesophase and that the micelles guided DNA migration. The effects of probe molecule charge on single-molecule diffusion within hexagonal STMS nanopores filled with cationic (R. Kumarasinghe, *et al.*, in prep.) and uncharged surfactants (S. C. Park, *et al.*, in prep.) were explored. The results show that the dimensionality and rate of motion are both charge dependent. The flow-induced alignment of CFBCP microdomains was investigated via the diffusion behavior of single molecules within the microdomains (K.-H. Tran-Ba, *et al.*, J. Phys. Chem. B. 2014, 118, 11406.). The results showed that alignment occurred by a shear mechanism and that micrometer sized grains limited long-range mass transport. Measurements of diffusion phenomena at both the ensemble and single-molecule levels in identical areas of nanostructured materials using FRAP and SMT (K.-H. Tran-Ba, *et al.*, in prep.) were demonstrated. Taken together, the ensemble and single-molecule results afford detailed data on the continuity of diffusion pathways. We have developed a new algorithm, trajectory-profile-guided tracking, that permits better assignment of one-dimensional single-molecule diffusion trajectories (K. C. Robben, *et al.*, Anal. Chem. 2014, 86, 10820.). Finally, we contributed invited review articles that comprehensively discussed analytical applications of block copolymer monoliths comprising microdomains (T. Ito, Chem.–Asian J. 2014, 9, 2708.) and single-molecule studies of morphology and mass transport dynamics within nanostructured materials (D. A. Higgins, *et al.*, Annu. Rev. Anal. Chem., submitted.).

The Physics and Chemistry of Cluster-Based Catalyst Systems

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Funding: \$316,274 (2014-2016)

PROGRAM SCOPE

We are carrying out theoretical/computational research that explores the physical and chemical properties of atomic clusters. Clusters are small clumps of matter containing from tens to hundreds of atoms and cluster science is a new frontier in the study of materials, spawning new ideas such as clusters as “superatoms” with an entirely new chemistry. Cluster properties are determined by an intricate interplay of factors related to their small size and can vary dramatically with the addition or deletion of even a few atoms. This sensitive size dependence creates the possibility of tailoring cluster properties for specific applications such as catalysis. The overall goal of our research is to use first-principles computational methods based on density functional theory (DFT) to gain an improved understanding of the properties of clusters, particularly those that are important for applications. The project has two main thrust areas: i) investigating the reactivity of metal and mixed-metal clusters that could be useful as catalysts; and ii) studying the polarizability of clusters as a function of the number of atoms in order to understand the evolution of electronic properties in matter at the smallest length scales.

FY 2014 HIGHLIGHTS

Our research resulted in three published papers. The first describes the chemical interaction between hydrogen molecules and palladium clusters. Dissociative adsorption occurs without barrier on these clusters. The second paper traces the evolution of cluster polarizabilities in Na clusters. We show that the charge transfer-type polarization is comparable to the bulk per atom value in clusters as small as 10 atoms. The final paper applies a new, linear response-based formalism that partitions the polarizability into atomic contributions to long-chain polymer molecules. Finite difference approaches cannot be applied to these systems.

- H₂ reactions on Palladium clusters. A. Pelzer, K. A. Jackson, and J. Jellinek, *J. Phys. Chem A*, v117, 10407 (2013).
- Investigating the metallic behavior of Na clusters using site specific polarizabilities. L. Ma, K. A. Jackson, M. Yang, J. Jellinek, and M. Horoi, *Phys. Rev. B* v89, 035429 (2014).
- Site-specific polarizabilities from analytic linear response theory. J. E. Peralta, V. Barone, and K. A. Jackson, *Chem. Phys. Lett.* v608, 24 (2014).

EARLY CAREER: Graphene Membranes with Tunable Nanometer-Scale Pores

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Funding: \$150,000 (2014)

PROGRAM SCOPE

Graphene, a one-atom thick membrane of hexagonally bonded carbon atoms, is one of the strongest materials known and is impervious to the diffusion of even helium gas. The potential for creation of tunable nanometer-scale pores in graphene, combined with its other properties, make it a promising

material for improving selectivity, permeability, and energy efficiency in a diverse range of membrane separation and sensing applications. The objective of this work is to systematically study the effect of ion irradiation, nitrogen doping, and chemical oxidation to create tunable, nanometer-scale pores in single and multilayer graphene membranes, and elucidate the transport characteristics of the resulting membranes. High-resolution imaging will be used to study the pore structures and transport measurements will be performed on large-area membranes as well as on single pores. The study will result in fundamental understanding of the relationship between fabrication methods, pore structures, and transport properties of graphene membranes, which may lead to significant advances in a wide range of separations applications.

FY 2014 HIGHLIGHTS

Development of leakage-sealing methods enabled measurements of water flux and solute transport across nanoporous monolayer graphene for the first time. The estimated flux of water through graphene pores was consistent with theoretical studies in the literature. Furthermore, the study demonstrated the ability of a single layer of graphene to filter out solutes (multivalent salts and small molecules). The filtration behavior was consistent with convection-diffusion model of mass transport across graphene pores, given the observed pore size distribution in graphene. Complementary to these studies with large area graphene membranes, studies of ionic conductance through isolated pores in graphene revealed ion-selective behavior and stochastic switching. A transport model was developed that accounted for electrostatic and ion hydration interactions. The model could quantitatively match the observed ionic conductance behaviors of isolated graphene nanopores.

Precisely tunable high performance carbon molecular sieve membranes for energy intensive separations

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Funding: \$120,000 (2014)

PROGRAM SCOPE

This project focuses on advanced carbon molecular sieve (CMS) membrane materials to dramatically reduce the energy intensity of gas separations. Polymer precursor dense films are being pyrolyzed to form materials with attractive properties. Fundamentally, we are seeking to show that constraining translational, rotational and vibrational degrees of freedom of the rejected components in the activated state reduce diffusion coefficients of the rejected component. Our preliminary experimental work supports the validity of this hypothesis and opens the way to progress toward economical advanced membrane materials. Besides the fundamental significance of the work, these findings also have enormous practical importance, since the work shows the way to develop processes for separating gas pairs at a greatly reduced energy cost. The polyimide precursor materials being study include trade-offs in segmental flexibility and packing, which allow structure-property insights to allow tunability for both smaller penetrant pairs like CO₂/CH₄ as well as the larger olefin-paraffin penetrants. These insights should provide the needed fundamental tools to tune ultra-micropore distributions to enable separations across the full spectrum of key gases needed for the next half century. Complementary studies, involving x-ray, thermogravimetric analysis assisted by mass spectrometry, Fourier transform

infrared spectroscopy and Raman spectroscopy will be used to gain additional fundamental insights into evolution of structures during the systematic formation work.

FY 2014 HIGHLIGHTS

Our earlier DOE BES work identified a so-called “entropic selectivity” principle that enables high performance membrane separation of the O₂/N₂ pair. Under our current DOE BES support, we have shown the validity of entropic selectivity as also crucially important for energy efficient separations of the N₂/CH₄ and the C₂H₄/C₂H₆ pairs. Both of these pairs are important in the hydrocarbon processing motivating the resurgence of the US economy. The CO₂/CH₄ case is another important gas pair related to enhanced oil production, which we are exploring to further assess our entropic selectivity factor analysis. Slit-like pores in CMS membranes enable such entropic selectivity factors to reduce overall energy intensity for all of above separations, which are currently done by highly energy intensive thermally-driven processes. Besides our theoretical work, our group has synthesized actual CMS membranes that demonstrate this special selectivity property. This work showed that CMS materials can undergo rapid physical aging, which is analogous to that observed with simple glassy polymers. Fortunately, under actual operating conditions we discovered that the aging in CMS materials is not a serious impediment to their practical use. Despite the ability to “live with aging”, during the past year, our group has begun exploring ways to slow down or even quench this aging process. We have already shown that selective trace level chemical treatments, which do not seriously impact the intrinsic productivity and selectivity of the CMS materials, are useful for control of the physical aging. This anti-aging work is ongoing, and will be pursued in the next grant period if the project is renewed.

The Dynamics and Thermodynamics of Gaseous Macro-ions

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Funding: \$165,000 (2014)

PROGRAM SCOPE

The overall objectives of this research effort are to expand the range of informative chemistries of gaseous polyatomic ions and their complexes within the context of a mass spectrometry experiment and to provide a deeper understanding of the factors that affect ionic reactions. The specific objectives of the project include study of the selective covalent bond in tandem mass spectrometry via ion/ion chemistry, which promises to greatly enhance the utility of structural characterization by tandem mass spectrometry, the study of ion/ion reactions involving non-covalently bound complex ions with emphasis on hydrated ions, and the spectroscopy of ions derived from energy relevant molecules, such as lignins.

FY 2014 HIGHLIGHTS

Cold Ion Spectroscopy and Photodissociation: We have made significant progress in our gas-phase ion spectroscopy collaboration with Professor Tim Zwiernicki in our department. We have constructed a triple quadrupole instrument with an ion optical axis that employs a multi-pole cold trap with a recirculating

liquid helium refrigeration system. This brings ions down to roughly 10 K so that we can generate high resolution infra-red spectra on conformation selected ions via an action spectroscopy approach. The instrument has been constructed and is generating data. We have collected both IR and UV spectra of well-studied systems, such as protonated tryptophan, and have begun generating data on ions derived from lignins, which are of interest to the bio-fuels community. Our first paper describing the lignin work has been submitted to the Journal of Physical Chemistry A. Selective Metal Ion Removal via Ion/Ion Reactions. We began a project this year involving the use of anions of superacids as ion/ion reagents in collaboration with Prof. Christopher Reed of UC Riverside. These ions have the interesting characteristic of being selective for metal ion removal when there is a mixture of metal ions and protons whereas virtually all other anions that we have used in the past are highly selective for proton removal. This interesting behavior is intimately linked with the low proton affinities of super acid anions. A paper is currently in press with the Journal of the American Society for Mass Spectrometry.

Imaging of Conformational Changes

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

Our ultimate objective is to develop methods for the detection and control of rotary conformational changes for single molecules in real time. In the initial funding period differential barrier height imaging (DBHI) and tip-enhanced resonance Raman spectroscopy (TERS) have been combined in a new instrument with the potential to make correlated maps of Raman band intensities and polarizations for molecules undergoing or having undergone electric-field induced conformational change. Tailor-made molecular rotors needed for the investigation have been prepared by standard methods of covalent synthesis, and new methods, developed by us, that substantially reduce the complication of the standard synthesis by using self-assembly. In several stages we will move from making a correlated map of the tunneling current, the DBHI plot and the static Raman spectra of single surface-mounted molecules to collecting dynamic Raman spectra of molecular rotors undergoing rotational conformational changes induced by the tip electric field. Raman spectroscopy is expected to quantify rotational conformational motion with up to 10-ns resolution in the dynamic investigations proposed here, and potential future ones with ps-time resolution. We believe this research will have represented a significant contribution to understanding of surface-enhanced Raman spectroscopy and single-molecule spectroscopic detection, both strong interests of the Separations and Analysis program of the Chemical Sciences, Geosciences and Biosciences Division, and towards the synthesis of solid-state materials with tailored properties from designed precursors, a strong interest of the Catalysis and Chemical Transformations program, also in the Chemical Sciences, Geosciences and Biosciences Division.

FY 2014 HIGHLIGHTS

Our target molecular rotor is a prismatic frame supporting a carbostyryl rotator. To avoid the standard covalent multistep synthesis of this compound, a two-step synthesis based on the convergent process of metal-ion-directed self-assembly was developed. To test the key covalent stabilization step, Pt(+)-N to

Pt-C conversion, simple squares were synthesized and confirmed by X-ray diffraction. The initial choice of trimethylphosphine as a ligand on Pt unfortunately permits a facile isomerization of the cis isomer into the trans isomer before covalent stabilization. A simple remedy was found by using a bridging diphosphine across two sites, preventing the rearrangement to the trans form. A model system containing a carbostyryl rotor derivative coupled by an axle to three fatty acid chains was synthesized to test for its TERS feasibility. This compound forms LB films neat or in dilution with stearic acid but segregates into islands. Ellipsometric, polarized FTIR, and UV-vis spectroscopic investigations of these rotor films showed that the rotor axle was unsuitably tilted. Further, the rotor was found to undergo dimerization in ambient light in the film. DBHI investigations on a series of rotors mounted on Au(111) were completed. A UV-TERS demonstration using a LB film of DiA was performed by excitation of a Co STM tip with 364 nm light and confirms that cobalt has a LSPR. This is the first time UV-TERS has been demonstrated with a Co tip. The near-field wavelength-dependent EM enhancement for a pair of cobalt spheroids was calculated using the discrete dipole scattering method. Two identical Co spheroids with a short axis of 40 nm and a 5 : 1 aspect ratio were placed perpendicularly separated by a 1 nm gap. A maximum enhancement factor >30 for the LSPR at 400 nm was found. A molecular dynamics simulation of molecular rotors driven by a rotating electric field or by a flow of gas was completed and provided insight into the nature of friction in molecular rotors.

The Flotation Chemistry of Nonsulfide Minerals

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Funding: \$480,000 (2014-2017)

PROGRAM SCOPE

Particulate separations are of considerable significance in many areas of technology ranging from pharmaceuticals and microelectronics, to mining and construction materials. In addition, particulate separation technology is of critical importance in the environmental area, for example the development of advanced water treatment processes for the 21st century will rely on more efficient particulate separation techniques. One such particulate separation process of considerable importance is the flotation separation process. The primary goal of this research program on flotation chemistry is to provide a basis for improved flotation separation efficiency in nonsulfide mineral systems by establishing the fundamental features of interfacial water structure, particle interactions, and collector (surfactant) adsorption reactions associated with the hydrophobic surface state and developing appropriate surface chemistry control strategies. Sum Frequency Vibrational Spectroscopy (SFVS), Molecular Dynamics Simulations (MDS), and Atomic Force Microscopy (AFM) are being used to accomplish this goal. These advanced experimental techniques together with more traditional experimental methods are providing crucial information concerning the interfacial surface state and collector adsorption phenomena in selected nonsulfide mineral systems, including, but not limited to, the flotation chemistry of phyllosilicate, soluble salt, and rare earth minerals in an effort to develop improved technology for the recovery of such strategic materials from our mineral resources.

FY 2014 HIGHLIGHTS

Flotation research activities in 2014 include the surface chemistry of layered silicate minerals and the rare earth mineral bastnaesite. Also, the spectroscopy of film rupture/bubble attachment is in progress. A significant achievement in the surface chemistry of phyllosilicates (layered silicates) has been accomplished. Namely, the experimental procedure for the isolation and preparation of the 30 nm thick edge surfaces of 300 nm anisotropic kaolinite particles has been successfully developed and the results published in JCIS, 420, pp. 35-40 (2014). These kaolinite edge surfaces have been characterized by AFM surface force measurements and the surface charge/surface potential calculated for the first time. Now, with these results, the interaction of such nano clay particles will be simulated in quantitative detail. Bastnaesite is a RE fluorocarbonate ($Ce,LaFCO_3$), and is an important domestic resource for RE production. Consequently, surface chemistry aspects of bastnaesite flotation with octyl hydroxamate collector are being studied. Advanced experimental techniques including collector adsorption experiments, sum frequency vibrational spectroscopy (SFVS) and molecular dynamic simulations (MDS) have been accomplished. The adsorption features as well as the corresponding hydrophobic surface state at low levels of hydroxamate adsorption had not been described. Finally, the presence of a water exclusion zone at hydrophobic surfaces has been established by MDS, X-ray reflectivity and SFVS. Further, it has been shown that the van der Waals (vdW) force between a bubble and such a hydrophobic surface is not repulsive as suggested in the literature. For example, even when the water exclusion zone is just 2 Å in thickness, an attractive vdW force is calculated and observed. As the thickness of the water exclusion zone increases, the calculated attractive vdW force increases, and helps to explain the nature of short-range and long-range hydrophobic forces.

Energetics of Nanomaterials

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

Nanomaterials differ in structure, reactivity, and thermodynamic properties from materials in the bulk. The focus of this project is the thermodynamics of nanomaterials, with synergy among three research groups: Brian Woodfield and Juliana Boreio Goates at Brigham Young University bringing expertise in nanoparticle synthesis and low temperature heat capacity measurements, Alexandra Navrotsky at University of California Davis bringing unique capabilities in high temperature calorimetry and the measurement of enthalpies of formation and surface energies, and Nancy Ross at Virginia Tech engaging in neutron scattering studies. Together this group seeks understanding of the systematics of surface energies and the hydration of nanoparticle surfaces and their effects on stability and reactivity. Current work has shown that different structures have systematically different surface energies, leading to crossover in thermodynamic stability of polymorphs at the nanoscale, and to substantial changes in the position of phase boundaries for dehydration and oxidation-reduction reactions. Such systematics are explored, with an emphasis on redox reactions and hydration. Studies of surface energies in spinel and

perovskite structures are performed and a useful set of surface energies for calculating nanoscale diagrams will be assembled. The details of structure and energetics of hydration layers are probed.

FY 2014 HIGHLIGHTS

Studies of bulk and nanophase spinels in the cobalt manganese oxide and iron manganese oxide systems confirm that the surface energies of all spinels in the systems are similar; thus the heat of mixing does not depend on particle size. The mixing energetics have been measured and modeled. The work is being prepared for publication. To explore new directions in nanoparticle energetics, which are highlighted in a submitted renewal proposal, we have studied several hybrid organic inorganic systems and their adsorption energetics of water and carbon dioxide.

Selected publications include:

- “Experimental Energetics of Large and Extra-Large Pore Zeolites: Pure Silica Beta Polymorph C (BEC) and Ge-containing ITQ-33” L. Wu, J. Hughes, M. Moliner, A. Navrotsky, and A. Corma, *Microporous Mesoporous Mater.*, 187, 77-81 (2014).
- “Energy Landscape of Self-Assembled Superlattices of PbSe Nanocrystals” Z. Quan, D. Wu, J. Zhu, W. H. Evers, J. M. Boncella, L. D. A. Siebbeles, Z. Wang, A. Navrotsky, and H. Xu, *Proc. Natl. Acad. Sci.*, 111, 9054-9057 (2014).
- “Energetics of CO₂ and H₂O Adsorption on Nano-ZnO Prepared by Laser Evaporation” D. Gouvea, S. V. Ushakov, and A. Navrotsky, *Langmuir*, 30, 9091-9097 (2014).
- “Energetics of Confinement of Hexane in Ca-Na Ion Exchanged Zeolite A” H. Sun, D. Wu, X. Guo, B. Shen, J. Liu, and A. Navrotsky, *J. Phys. Chem.*, 118, 25590-25596 (2014).
- “Thermodynamics of Metal-Organic Frameworks” D. Wu and A. Navrotsky, *J. Solid State Chem.*, In Press (2014).
- “Thermodynamic Stability and Correlation with Synthesis Conditions, Structure and Phase Transformations in Orthorhombic and Monoclinic Li₂M(SO₄)₂ (M = Mn, Fe, Co, Ni) Polymorphs” A. V. Radha, L. Lander, G. Rousse, J.-M. Tarascon, and A. Navrotsky, *J. Mater. Chem. A*, In Press (2014).

Hyperthin Membranes for Gas Separations

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Funding: \$465,000 (2014-2017)

PROGRAM SCOPE

This research focuses on the design, synthesis and characterization of hyperthin (< 100 nm) polymeric membranes based on polyelectrolyte multilayer (PEM) formation and Langmuir-Blodgett (LB) deposition. This work builds upon two recent discoveries: (i) unexpectedly high CO₂/N₂ permeation selectivities that have been found for PEMs made from two commonly used polyelectrolytes, and permeances that were two to three times greater for structurally matched analogs, and (ii) A 7 nm-thick Langmuir-Blodgett bilayer derived a polymeric surfactant (POMTMA) plus poly(acrylic acid) having a H₂/CO₂ selectivity of 200 that reached the “upper bound”². This research will explore the scope of structural matching of polyelectrolytes as it relates to its influence on the permeation properties of

resulting PEMs. Specifically, the consequences of hydrogen bonding, the position of the pendant ions along the polymer backbone, and polymer tacticity on the barrier properties of PEMs will be determined with respect to H₂, CO₂ and N₂. Related studies will test the feasibility of introducing uniform micropores into PEMs to produce relatively fast selective gas transport. Finally, the influence that covalent crosslinking has on the permeation properties and robustness of PEMs and ionically crosslinked, all-polymer-based-LB bilayers will be examined. At a fundamental level, the concept of structural matching is entirely new in the PEM area. As further advances are made with hyperthin PEMs as membrane materials, sensors, protective coatings, etc., the results of this research should provide valuable insight into what possibilities may exist for further development through structural matching.

FY 2014 HIGHLIGHTS

Polyelectrolyte multilayers derived from poly(diallyldimethylammonium chloride) and poly(sodium 4-styrene sulfonate) have been deposited onto poly[1-(trimethylsilyl)-1-propyne] (PTMSP) with anchoring layers formed by Langmuir-Blodgett and self-assembly methods. Using gas permeation selectivity as a basis for judging the efficacy of each anchoring method, we have found that similar CO₂/N₂ selectivities (ranging from 110-140) could be achieved by both methods, and that their permeances were also similar. Although LB anchors require fewer layers of polyelectrolyte to reach this level of selectivity, the greater ease associated with self-assembly, and its applicability to curved, high surface area supports (e.g., PTMSP-coated hollow fibers), encourages its use with PTMSP in creating new membrane materials for the practical separation of gases.

Developing Ion Mobility-Mass Spectrometry for Structural Characterization of Complex Molecular Systems

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Funding: \$170,000 (2014)

PROGRAM SCOPE

Our research focuses on developing mass spectrometry-based approaches for determining the structure(s) of molecules and molecule complexes and how structure influences reactivity. Our studies employ a variety of cutting-edge mass spectrometry instrument types and structural probes, ranging from ion-neutral and ion-surface collisions, e.g., collision-induced dissociation and surface-induced dissociation and electronic excitation, including electron-capture and electron-transfer dissociation. These structural probes are combined with ion mobility-mass spectrometry (IM-MS), which separates ions on the basis of size-to-charge. There is natural synergy between size- and m/z-based separation and resulting structural information, and the ability to experimentally determine the heterogeneity (structural diversity) of the ion population, which affords separation of isomeric species. Molecular dynamics (MD) simulations are integral to IM-based structure determination, i.e., structure is not derived from first principles. Consequently, a significant component of our research involves computation and informatics. During the last two years we have used IM-MS and MD simulations to understand the structure of water, viz. ions of the type H⁺(H₂O)_n, where n ranges from 0 to >100, and

similar hydrates of polar molecules, $[M + H]^+ \cdot (H_2O)_n$. These focus on understanding how water influences the structure of the M as well as how M influences the structure of water.

FY 2014 HIGHLIGHTS

Our most important accomplishment this year has been in developing a more thorough understanding of the effects of water on conformational preference and dynamics of peptide using cryogenic (80 K)-ion mobility-mass spectrometry (cryo-IM-MS). Cryogenic-IM-MS makes possible novel investigations of ionic water clusters and hydrated polar molecules. In the course of these studies we have provided new insights on the structure of hydrated protons and hydronium ions, specifically how the structures of the hydrated species change with the extent of hydration. We have also shown how hydration affects the structures of hydrated peptides as well as how this experiment can be utilized for “kinetic trapping” of specific conformers for systems where multiple conformations are energetically possible. Five publications in high impact journals have been derived from these studies. We have also developed new IM-MS approaches for deconvolution of complex tandem MS spectra, and we have demonstrated the utility of these approaches through collaborations with biological and materials chemists, which amply illustrate the broader impact of the research. This work clearly illustrates that IM-MS is rapidly evolving as one of the most versatile and information-rich mass spectrometry-based analytical techniques. In many of the challenging areas of 21st century chemical research, the needs for rapid, high-throughput, ultra-high sensitivity analytical techniques continue to grow. Such experimental capabilities are now spilling over into diverse areas including catalysis and nano-catalysis, polymer/materials science, petroleomics, esp. bio-mass/biofuels and renewable energy.

EARLY CAREER: A Physicochemical Method for Separating Rare Earths: Addressing an Impending Shortfall

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Funding: \$150,000 (2014)

PROGRAM SCOPE

The broad aim of this project is to develop and apply fundamental chemistry to the separation of mixtures of rare earth metals. We are developing coordination chemistry of rare earth metal cations, including La–Pr, Tb, and Dy in an effort to connect meaningful chemical properties that can be used for elemental separations with their distinctive electronic structure characteristics. Our hypothesis for the project is that electron-hole coupling (electronic configurational mixing) in molecular complexes of certain lanthanide metals with redox active ligands can be used to manifest chemical distinctiveness and affect separations. The study of such effects also expands the basic knowledge of f-element chemistry and electronic structure. New redox active nitroxide ligands are proposed to both bind the rare earth cations and to observe electronic/magnetic coupling and redox chemistry between metal 4f electrons and ligand electron-holes. We expect that the redox active ligands will affect selective complexation of specific rare earth metal cations in mixture depending on the electronic characteristics of the ligands. The electronic structure effects discovered will be used as design principles for tailored extractants for

use in liquid-liquid extraction or other separations techniques for superior performance over extractant schemes currently in use.

FY 2014 HIGHLIGHTS

Our efforts to study metal-ligand redox have been applied to two processes in the rare earth metals supply chain. We have isolated a cerium(IV) hydroxamate complex in the context of beneficiation of rare earths ores. Beneficiation by froth floatation is the first step for claiming rare earths from ores. Crushed rare earth mineral solids are separated from waste materials through surface chemistry of organic 'collectors,' such as hydroxamates. Our analysis of the Ce-hydroxamate complex showed a strong preference for the cerium(IV) state. These results indicated that engineering models of beneficiation must include redox chemistry, which we expect will contribute to improved efficiency in this critical process. We have also leveraged computations to study metal redox processes. An experimental/computationally-predicted correlation of the redox properties for 15 cerium complexes has been achieved. Starting from crystal structures, density functional theory was applied to compute energies for the compounds in both multiple redox forms. Comparison the results with the experimentally measured values produced an excellent correlation with a range of more than 2.5 V. We expect this approach will find broad application in separations, including the design of chemical systems for lanthanide/actinide separations. Multi-dentate nitroxide ligands have been synthesized and their coordination chemistry with the lanthanides launched. A tripodal ligand framework was expected to provide a binding pocket for controlled coordination chemistry within an open coordination site. We have achieved the synthesis of a tripodal nitroxide ligand: $((2\text{-tBuNOH})\text{C}_6\text{H}_4\text{CH}_2)_3\text{N}$ (H_3TriNO_x), and its coordination to a rare earth cation to form complexes: $\text{RE}(\text{THF})(\text{TriNO}_x)$ RE = rare earth metal. The $\text{RE}(\text{THF})(\text{TriNO}_x)$ complexes have unusual isomeric- and solubility-properties. We have leveraged these observations to affect simple separations of pairs of rare earth ions, an approach that was recently patented.

Surface Functionality and Reactivity Using Single-Molecule Probes

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Funding: \$216,664 (2014)

PROGRAM SCOPE

The goal of this project is to develop and employ real-time imaging methods that use individual reactant/adsorbate molecules as probes of surface chemical functionality (particularly non-covalent interactions) and reactivity. Our approach is based on observations of individual molecules using total internal reflection fluorescence microscopy (TIRFM), including high-resolution spectral methods involving resonance energy transfer. Methods like these will be necessary for the development and characterization – and especially the mechanistic understanding – of patterned and/or self-organized nanomaterials as well as of advanced catalysts that modify the environment of the active site (using non-covalent interactions) to improve reactivity, selectivity, and longevity.

FY 2014 HIGHLIGHTS

We have developed methods to study heterogeneous surface properties using the dynamic behavior of multiple probe molecules that respond to different chemical surface properties. Using diffusion, adsorption rate, and residence time from both probes allows the use of an unsupervised 6D Gaussian mixture model to identify data clusters corresponding to individual surface chemistries, which can then be mapped back onto the surface spatially. We also connected single-molecule dynamic observations directly with retention times in reversed phase liquid chromatography (RPLC). Using the dynamic behavior of individual probe molecules we identified strong surface binding sites. The adsorption and desorption kinetics on these sites were heterogeneous and positively correlated, suggesting a broad underlying distribution of site binding energies. Using the stochastic model of chromatography, we showed that single-molecule kinetic results were consistent with the empirical trend observed in actual RPLC experiments as a function of the solvent composition. This approach to identifying and quantifying adsorption sites should be useful for designing better chromatographic separations and for identifying the role of heterogeneous surface chemistry in molecular dynamics. In the conventional picture of surface diffusion, a molecule sticks to a surface and moves continuously following a two-dimensional random walk. However, in recent experiments, we observed stop-and-go hopping across the surface with a diverse group of molecules. The molecules underwent periods of confined 2D diffusion punctuated by occasional long 3-dimensional flights. These trajectories, similar to “forager dynamics” well-known in biology, represent a highly efficient search process. This conceptual understanding also enabled new insights into polymer surface dynamics. These findings may enable new approaches to control or direct molecular motion at interfaces.

New Approaches for Metabolomics by Mass Spectrometry

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Funding: \$330,000 (2013-2014)

PROGRAM SCOPE

Small molecules constitute a large part of the world around us, including fossil and some renewable energy sources. Solar energy harvested by plants and bacteria is converted into energy rich small molecules on a massive scale. Some of the worst contaminants of the environment and compounds of interest for national security also fall in the category of small molecules. The development of large scale metabolomic analysis methods lags behind the state of the art established for genomics and proteomics. This is commonly attributed to the diversity of molecular classes included in a metabolome. Unlike nucleic acids and proteins, metabolites do not have standard building blocks, and, as a result, their molecular properties exhibit a wide spectrum. This impedes the development of dedicated separation and spectroscopic methods. Mass spectrometry (MS) is used as a quantitative analytical tool with extensive metabolite coverage. Although various MS-based techniques are emerging for metabolomics, many of these approaches include extensive sample preparation that make large scale studies resource intensive and slow. New ionization methods are redefining the range of analytical problems that can be solved using MS. This program aims to develop new approaches for the direct analysis of small molecules in unprocessed samples, as well as push the limits of ultratrace analysis in volume limited

complex samples. These projects will result in techniques that enable metabolomics investigations with enhanced molecular coverage, as well as the study of cellular response to external perturbation. We established a new analytical platform, laser ablation electrospray ionization (LAESI) in combination with ion mobility separation (IMS) and MS, for the direct study of metabolic changes in cells and tissues following external perturbation.

FY 2014 HIGHLIGHTS

During the reporting period we demonstrated the utility of LAESI-IMS-MS to directly identify metabolites and lipids in genetically modified energy harvesting green alga (*Chlamydomonas reinhardtii*) under altered light conditions. To determine the turnover rate of secondary metabolites, lipids and peptides, we introduced pulse-chase experiments based on stable isotope labeling in combination with LAESI-IMS-MS. Increased lipid yields were observed in genetically modified strains of *C. reinhardtii*. Wild type (WT) and several mutants of *C. reinhardtii* were raised in tris-acetate phosphate (TAP) medium. Compared to the WT, an impaired starch pathway mutant showed a higher production of triacylglycerol (TAG) and digalactosyldiacylglycerol (DGDG) lipids under both light and dark conditions. LAESI-IMS-MS showed the presence of particular TAGs in both conditions, proving this to be an efficient technique for rapid lipid identification. To explore the turnover rates of the abundant diacylglyceryl-N,N,N-trimethylhomoserines (DGTS) in *C. reinhardtii*, it was cultured in ¹⁵N-labeled TAP (pulse phase). For the chase phase the ¹⁵N-labeled TAP was replaced with ¹⁴N-TAP. At several time points, analysis was conducted to discern turnover rates and half-lives of nitrogen containing biomolecules, e.g., essential lipids. LAESI-MS in combination with stable isotope pulse-chase experiments promises to provide a rapid assessment of metabolic conversion rates in complex biological systems. Extended molecular coverage in direct analysis of biological samples, e.g., the model plant *Arabidopsis thaliana*, was achieved by collecting both positive and negative ion LAESI-IMS-MS spectra and by introducing reactive components into the electrospray. In negative ion mode LAESI-IMS-MS for the analysis of *A. thaliana* leaves, small metabolites, glucosinolates (plant defense compounds), phosphatidylglycerols and triglycerides were simultaneously detected.

Computer Simulation of Proton Transport in Fuel Cell Membranes

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

This project involves a unique multiscale computer simulation methodology for studying proton solvation and transport in proton exchange membranes (PEMs) for fuel cell applications. A key component of the project is a novel atomistic molecular dynamics (MD) simulation approach called the Self-Consistent Iterative Multi-State Empirical Valence Bond (SCI-MS-EVB) method, which has provided, for the first time, an atomistic simulation capability to study excess proton solvation and transport in PEM, including the critical Grotthuss shuttling process (hopping transport) and vehicular transport (classical Einstein diffusion) on the same footing. Several significant advances of the SCI-MS-EVB approach have been made to improve efficiency and will be extended in the future, including a force-

matching method to derive accurate SCI-MS-EVB model parameters from *ab initio* molecular dynamics (AIMD) simulations. These algorithmic advances and enhanced code scalability have further allowed the SCI-MS-EVB simulations to access increasingly large system sizes and long simulation times. Key results obtained during the past funding period have revealed the remarkably complex behavior of the proton solvation and transport in the hydrophilic domains of Nafion™, including an unusual and unexpected anti-correlation between vehicular transport and hopping transport which increases with decreasing PEM hydration levels. The water properties in various proposed Nafion morphological models have been investigated in large-scale MD studies in order to understand how proton transport is influenced by both hydration and morphology. Novel mesoscopic-scale simulations of proton transport in PEMs have also been developed, with key extension proposed, that include a multiscale bridging of the atomistic SCI-MS-EVB data to mesoscopic proton transport modeling coupled to complex PEM morphology.

FY 2014 HIGHLIGHTS

To understand the fundamental mechanism of proton transport within perfluorosulfonic acid (PFSA) membranes, we have utilized extensive large scale SCI-MS-EVB simulations to examine two PFSA materials, Hyflon and the 3M membrane, at different hydration levels. Specific interactions between the sulfonate groups of the polymer side chains and the hydrated protons were found to have a relatively limited influence on the proton transport. Instead, proton swapping between the close hydration layers of the sulfonates was the primary mechanism for the proton transport. The hydrated excess protons are essentially always within two solvation shells of the sulfonate groups. When the solvation shells of neighboring sulfonate groups can overlap substantially, the depth of the potential energy well of individual sulfonates becomes less important. The hydrated excess proton can transfer to an adjacent, overlapping potential well, if and there is an adjacent sulfonate group. The larger water clusters and more flexible side chain of the 3M membrane allow for an enhancement of this swapping mechanism compared to Hyflon. These results have been made possible by recent advances in our SCI-MS-EVB approach, which is a unique computational methodology. It has also been found that the caging effects for the proton transport in the PFSA materials lasts up to at least 1 ns and so the required time scale for a proper calculation of the proton self-diffusion constant cannot be shorter than around 10 ns. This finding demonstrates that multiple SCI-MS-EVB trajectories of at least several nanoseconds long are needed in order to fully characterize the long-time behavior of proton transport in PFSAs, well beyond the current capabilities of *ab initio* molecular dynamics simulation.

Subnanometer Spatial Resolution Chemical Imaging

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Funding:	\$630,000 (2014-2017)

PROGRAM SCOPE

We develop submolecular-resolution spectroscopic imaging in the visible, near-visible, and vibrational infrared ranges. These scanning tunneling microscopes (STMs) are used for chemical imaging in order to measure structure, function, and spectroscopy simultaneously. By combining these measurements we

will develop enabling tools to elucidate the nanoscale rules of function at the ultimate limits of miniaturization.

FY 2014 HIGHLIGHTS

We have induced (the first recorded) cooperative motion in precisely assembled one-molecule-wide lines of azobenzene-functionalized molecules. This motion has been induced both with ultraviolet (UV) photons in “broadcast” mode and locally with electrons of substantially lower energy, supplied by the STM probe tip. New capabilities were developed in order to induce this cooperative motion. First, we developed the means to assemble one-dimensional lines of functional molecules along domain boundaries in self-assembled monolayers. After our initial observation that this was possible, we were able to make these one-dimensional lines dominate the assembly of the functional molecules by processing the co-assembled films. We also developed the means to record the motion with both spatial isolation and spectral isolation, with scanning tunneling microscopy and plasmonic-substrate-enhanced Raman spectroscopy. In combination with theoretical calculations and spectroscopic simulations, we were determined that electron delocalization along the chains is critical to cooperative function in this case and were able to determine the mechanism(s) of isomerization.

Chemical Imaging with Cluster Ion Beams and Lasers

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PROGRAM SCOPE

This research effort with the Department of Energy is focused upon the use of cluster ion bombardment of surfaces, followed by laser photoionization of desorbed neutral molecules, for molecule-specific imaging experiments. This unique strategy allows the chemical identification of small molecules in the near surface region of a solid to be mapped with a lateral resolution of a few hundred nanometers, and a depth resolution of about 10 nm. The basic idea is to utilize an energetic cluster ion beam, consisting of C₆₀ or Ar₄₀₀₀ molecules, that is focused to a well-defined point on the target. During the energy deposition process, both the neutral and ionized molecules are desorbed from the surface. This research is aimed toward finding novel ways to ionize the neutral molecules using suitable a suitable light source to enhance the sensitivity to allow improved imaging and to produce as little photo-induced fragmentation as possible. The photoionized molecular ions are detected by time-of-flight mass spectrometry, and an image is created by scanning the ion beam over an appropriate area. The overarching goal is to broaden the scope of mass spectrometry imaging experiments through techniques aimed to improve molecular desorption efficiency and instrumental sensitivity.

FY 2014 HIGHLIGHTS

Prior DOE-funded research has led us to utilize high field femtosecond IR pulsed laser radiation for the most efficient photoionization of sputtered molecules. The use of IR radiation is important in order to reduce photo-fragmentation by increasing the probability of ionization via a tunneling mechanism rather

than by multiphoton excitation. A unique laser system has been implemented in the laboratory, which produces 40 fs pulses throughout the near IR (1200 nm – 2000 nm) with a peak power density approaching 1 petawatt, and a pulse repetition rate of 1 kHz. Protocols have been developed for maximizing the ionization efficiency by systematically varying laser intensity, wavelength and polarization. During FY 2014, our group has focused upon the demonstration of this strategy using a wide variety of target molecules, and to determine whether this approach does indeed improve the sensitivity of the mass spectrometry measurements. The results have been quite spectacular since we have been able to efficiently photoionize molecules up to molecular weights of nearly m/z 1000, a result not yet obtained using any other laser photoionization approach. Moreover, we have demonstrated that the method is useful for a broad range of molecules including long chain fatty acids, cholesterol and other sterols, aromatic hydrocarbons, sugars, and a variety of metal-organic compounds. Molecule-specific images have been obtained from biological tissue sections and from single algae cells. The algae studies are quite interesting since we find localization of hydrocarbons (squalene in particular) within globules produced inside the cell. With this information and the enhanced sensitivity of our imaging approach, we can better speculate about how these cells produce hydrocarbons, and hence, how their energy production might be improved. The results have been published in a series of 3 papers in Analytical Chemistry and in The Journal of Physical Chemistry.

DOE National Laboratories

Fundamental Studies of Novel Separations

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Funding: \$825,000 (2014)

PROGRAM SCOPE

The overall goal of this project is to investigate fundamental issues of gas separations by nanostructured architectures and unconventional media that selectively bind and/or transport target molecular species via tailored interactions. To achieve this goal, we will pursue three specific aims: (1) How do the molecular structures of ionic liquids (ILs) dictate separations in gas/ionic liquid systems to achieve high selectivity and fast diffusivity? (2) How do the porosity and nitrogen functionality of carbonaceous materials control gas adsorption and diffusion for advanced separations? (3) How can porous carbon and ionic liquids be rationally integrated to create advanced separation materials with controlled porosity and functionality, fast transport, and high selectivity? A combination of synthesis, characterization, testing and modeling will be employed to answer these questions. More specifically, we will explore how the molecular structure and functionality of ILs and/or combinations of ILs impact both gas solubility and diffusivity. Through improved understanding of the impact of gas/IL and cation/anion interactions and the effect of these interactions on solubility and diffusivity, we will improve our ability to design liquid membrane systems with enhanced permeability and permselectivity. We will explore novel methods to control both the surface functionality and porosity of carbon membranes to further elucidate the precise mechanisms that control gas adsorption and transport. Finally, we will take advantage of the unique properties of porous materials and ILs to create porous

liquid systems that will enhance both gas diffusivity and permselectivity in integrated membrane systems. Though we primarily focus on CO₂/N₂ separation, this work will be applicable to other species and also in developing advanced separation media which hold the key to future chemical separations in energy production and utilization, environmental remediation, and carbon capture.

FY 2014 HIGHLIGHTS

A porous, triazine and carbazole bifunctionalized task-specific polymer was synthesized via a facile Friedel–Crafts reaction. The resultant porous framework exhibited excellent CO₂ uptake (4.1 mmol/g at 273 K and 1 bar) and good CO₂/N₂ adsorption selectivity. The synthesis of hierarchical macro-, meso-, and micro-porous polymeric molecular sieve membranes was demonstrated using a one-step, *in situ* cross-linking process based on the Kirkendall effect. The porous polystyrene membranes exhibited high permeability and selectivity promising for gas separations. A CO₂-philic amidoxime functional group was grafted onto a porous carbon framework for the selective capture and removal of carbon dioxide. The presence of the amidoxime group enhanced CO₂/N₂ selectivity due to a stronger interaction of CO₂ with the functional group. Free-standing mesoporous carbon-graphitic carbon nanocomposite membranes with controllable pore size (7.3-11.3 nm) were synthesized by the “brick-and-mortar” method, in which carbon black (CB) serves as the “bricks” and soft-templated phenolic resin-based mesoporous carbon (MC) serves as the “mortar”. Immobilization of ionic liquids in the carbon gave highly stable supported ionic liquid membranes at more than 10 atm transmembrane pressure. Mesoporous carbons were prepared via spinodal decomposition of non-amphiphilic linear polyethylene glycol with phloroglucinol–formaldehyde resin under refluxing acidic ethanol conditions. By shifting the molecular weight and the concentration of the polyethylene glycol, both mesopore size and volume could be tuned.

Chemical Analysis

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Funding: \$853,000 (2014)

PROGRAM SCOPE

The goal of our research is to obtain a fundamental understanding of the physical phenomena underlying chemical analysis of molecules and small particles in complex, heterogeneous environments. To achieve this goal we develop unique mass spectrometry instrumentation for studying ion-surface collisions and for comprehensive physical and chemical characterization of small particles. These one-of-a-kind experimental tools are used to address analytical challenges of interest to catalysis, energy storage, materials science, and environmental science. Specifically, our experiments probe physical and chemical phenomena underlying collisions of ions with surfaces. Surface induced dissociation provides important information on the binding energies in complex molecules of interest to self-assembly, photovoltaics, and light harvesting. Our fundamental studies established preparatory mass spectrometry as a unique tool for the highly selective preparation of novel materials. We also develop nanospray desorption electrospray ionization– a new ambient ionization technique for sensitive chemical analysis of complex mixtures. Our experimental capabilities enable multidimensional characterization of a of

individual small particles in-situ and in real-time. Simultaneous measurements of particle, size, composition, density, shape, phase, and fractal dimension transformed the way complex organic particles are viewed and treated by models. Specifically, we demonstrated that evaporation rates of mixed organic particles are orders of magnitude slower than predicted by broadly accepted models indicating these particles are semi-solids. Using the newly developed methods to characterize particle morphology, we demonstrated the multi-layered structure of complex organic particles. Unique software packages were developed for visualization and interpretation of the large experimental datasets without loss of detailed information that is inherent to multidimensional individual particle data.

FY 2014 HIGHLIGHTS

Surface-induced dissociation experiments enabled the first experimental determination of the ligand binding energies in small triphenylphosphine-ligated cationic gold clusters. We demonstrated that clusters with high ligand binding energies are observed with enhanced abundance in the initial stages of nucleation in solution. These results are important to controlling solution-phase nucleation and growth of nanoparticles of interest to catalysis, molecular electronics, and sensing. We also developed a new temperature-controlled flow reactor for studying nanoparticle formation in solution using mass spectrometry, which will enable future studies of the structures and stability of intermediates produced during batch synthesis. Our soft-landing experiments focused on charge retention by native dications and anions on well-characterized organic surfaces. Fundamental understanding of charge retention is essential for the controlled preparation of catalytically active substrates using ion soft-landing. Our studies of phenomena pertinent to the non-equilibrium formation, properties, and transformations of complex organic-containing particles, focused on understanding diffusion in nanoparticles, characterization of particle morphology, and evaporation kinetics of size-selected nanoparticles at different relative humidity. Imaging of particles with multifaceted shapes and morphologies provided important information on the relationship between nanoparticle shapes, physicochemical properties, and dynamics in different flow regimes. In addition, we continued the development of new approaches for visualization and analysis of large multidimensional data. Specifically, we implemented a novel approach to incremental correlation clustering of large datasets with visual feedback, and new interactive visual analytics software designed to explore and visualize complex, multidimensional data in a geo-spatial context.

Principles of Chemical Recognition and Transport in Extractive Separations

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Funding: \$1,135,000 (2014)

PROGRAM SCOPE

This program strives to provide new understanding of the theoretical, synthetic, structural, and thermodynamic principles of molecular recognition leading to unprecedented selectivity and control of

ion binding in separations such as liquid-liquid extraction and crystallization. The major line of inquiry deals with the design of fully functional ion receptors that can completely accommodate the coordination and charge-neutralization requirements for separation of ions, ion pairs, or ion aggregates, whether the recognition occurs with discrete molecular receptors or small molecular units that function by self-assembly. Three specific aims deal with computer-aided molecular design to guide the discovery of molecular structures with controlled functionality; self-assembly of small molecular units with multiple ions to form predetermined structures; and cooperativity effects in the selective separation of ions and ion pairs. Specific progress is being made with new anion-binding motifs based on new guanidinium, urea, and calixpyrrole platforms, and when these are combined with cation-binding groups, the resulting ditopic structures self-assemble with ion-pairs in high-order assemblies. Resulting transformative understanding of the theoretical, structural, and thermodynamic principles underlying ion recognition will strongly benefit DOE's energy, environmental, and national-security missions.

FY 2014 HIGHLIGHTS

Research results in FY 2014 reflect an advancing understanding of fully functional receptors for selective separation of ions in extractive systems. Most newsworthy was the first demonstration of a pseudobicyclic guanidinium receptor for binding oxoanions. The guanidinium group has long been a key building block in the design of oxoanion receptors, but its flexibility has led researchers to employ a difficult-to-prepare bicyclic guanidinium structure for preorganization. To explore whether alternative pseudobicyclic analogs could be found, N,N'-bispyridylguanidine was successfully synthesized, and an X-ray crystal structure demonstrated the 2:1 symmetrical binding of sulfate by the hypothesized pseudobicyclic guanidinium form. In another major accomplishment, the use of an anion receptor, meso-octamethylcalix[4]pyrrole (C₄P), to alter the selectivity of liquid-liquid cation exchange was demonstrated for the first time, and a crystal structure confirmed the hypothesized binding of the lipophilic anion of the alkylphenol cation exchanger by C₄P. To improve the solubility of C₄P in organic solvents, the template synthesis of a tetrahexyl derivative was accomplished in a single pot, and the new more lipophilic derivative serendipitously exhibited 100-fold greater selectivity for sulfate vs. chloride in an anion-exchange system. Extraction of sulfate by two bispyrrole-strapped C₄P anion receptors provided by collaborator J. L. Sessler at UT-Austin was also elucidated. In preparation for ion-pair extraction studies of Fr⁺ ion using C₄P, the Gibbs energies of partitioning of Fr⁺ between water and the solvents 1,2-dichloroethane and o-nitrophenyl octyl ether were determined for the first time. The molecular design of ion-pair architectures, including helicates and higher-order assemblies such as cubes and tetrahedra was completed, and preliminary results were obtained for the self-assembly of one of the targeted structures in solution.

Laser Materials Interactions (Ablation)

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Funding: \$340,000 (2014)

PROGRAM SCOPE

Traditional chemical analysis involves outdated laborious acid dissolution procedures that are harmful to personnel and the environment. In contrast, laser based chemical analysis offers a clean (green) advanced capability that mainly utilizes light energy. The research in this BES program focuses on understanding and developing laser ablation for direct solid sample chemical analysis; laser ablation offers real-time analysis without sample preparation or consumables, provides nanometer spatial scale imaging and analysis, and can be utilized for every application, for example energy, environmental, forensics, nonproliferation and almost every industrial application. Laser ablation chemical analysis can and will become a mainstream capability for society by expanding our knowledge of fundamental processes; establishing underlying principles for using laser energy to measure the chemistry of a sample. This research emphasizes the study of laser ablation for elemental and isotopic analysis at atmospheric pressure. Goals are to understand fundamental principles related to the efficiency of coupling laser energy into the sample, energy transfer, thermal and shock removal of sample constituents during ablation, effect of ionized plasma shielding, the influence of the surface plasma on ablation, and particle formation. The research also addresses laser plasma chemistry as the fundamental basis for formation of chemical species in the plasma plume that ultimately influence the precision and accuracy of analysis. Time-resolving underlying non-linear ablation processes and assigning mechanisms to describe the measured chemistry in the plasma and of the aerosol form the basis of this research program.

FY 2014 HIGHLIGHTS

Our recent breakthrough in this laser ablation chemical analysis technology was the discovery of molecular signatures in the optical surface plasma (induced by the laser ablation event) that amplify spectral isotope splitting; molecular bands provide isotope signatures with orders of magnitude spectral splitting compared to atomic and ionic lines. Our new technology was named LAMIS for Laser Ablation Molecular Isotopic Spectroscopy. LAMIS provides new capabilities for studying laser ablation processes and as a new technology for real time isotopic analysis without a mass spectrometer. The LAMIS technology has won several awards including twice being recognized as best published papers in Spectrochimica Acta B. Using isotopically spiked samples, we measured the spatial and temporal formation of molecular species in the plasma, and related these data to the underlying high temperature and pressure ablation of the sample. These new data allow us to tailor the ablation process for enhancing the sensitivity, accuracy and precision of analysis. We demonstrated LAMIS as a new isotope analysis technology with precision approaching that of thermal ionization mass spectrometry (TIMS) for boron isotope ratio measurements. The LAMIS data were recorded at atmospheric pressure in two minutes whereas the TIMS data required vacuum, sample preparation and almost two hours. To date, we have demonstrated LAMIS for U, Sr, W, H/D and C. Precision is dependent on the number of laser pulses; we have achieved <0.1% precision using 1000 laser pulses (two minutes). LAMIS is gaining recognition by the analytical scientific community as one of the most significant capabilities presented in atomic spectroscopy.

Chemical Analysis of Nanodomains

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Funding: \$582,000 (2014)

PROGRAM SCOPE

Many important phenomena occur on a spatial scale that is smaller than can be probed noninvasively by conventional optical techniques. Understanding these nanoscale phenomena is fundamental to the DOE mission of developing new and revolutionary clean energy technologies. Using the combined tools of time-resolved stimulated emission depletion (fluorescence) microscopy, scanning angle (SA) Raman microscopy, time-resolved spectroscopies, and skills in materials synthesis, the Chemical Analysis of Nanodomains program develops and characterizes distinct and widely applicable strategies for preparing nanomaterials and films of nanomaterials having improved performance in solar cells. The objective of the research is the analysis of the next generation of solar-cell materials that will one day outperform existing commercial technologies in terms of efficiency, stability, and cost. The specific aims are to: (1) develop and elucidate the photophysical, photochemical, and stability behavior displayed by organometal halide perovskite and germanium nanomaterials; (2) develop SA Raman spectroscopy to extract axial chemical information about films consisting of two or more species with distinct layers or phases; (3) develop a fundamental understanding of the diffusion properties within a polymer film containing defined structural characteristics; and (4) identify the structural features responsible for performance decay and enhancement in organometal halide perovskite and germanium solar cells. As outlined in the BESAC report, "New Science for a Secure and Sustainable Energy Future," this work fills a need for the development of teams "to close gaps between needs and capabilities in synthesis [and] characterization ... of advanced materials," and develop tools that probe materials and chemical processes with unprecedented resolution, where the compositions and dynamics need to be non-invasively measured on the nanoscale, and particularly for analyses in complex environments.

FY 2014 HIGHLIGHTS

Stimulated Emission Depletion (STED) Imaging: This program quantitatively addressed how to increase the validity of measured lifetimes by STED without compromising the subdiffraction spatial resolution, which is the inherent benefit of the technique. The important conclusion of this work is time binning can be applied to increase the number of photons in the peak channel without affecting the lifetime values.

SA Raman Spectroscopy: A second-generation, fully automated, low angular spread and uncertainty, visible excitation SA Raman spectrometer was developed. SA Raman spectra of a diblock copolymer were collected with a signal-to-noise ratio of 30 using a 0.25 s acquisition. The instrument was subsequently used to study bulk heterojunction photostability of organic photovoltaic films containing a polymer donor and a fullerene-derivative acceptor. This information can enable more photostable devices, with the end goal of providing organic photovoltaic films suitable for a range of applications. A complementary technique for thin film analyses at a gold interface called Fourier transform plasmon waveguide resonance was also demonstrated; and the location of a buried interface between two polymers was measured by SA Raman spectroscopy with approximately 10 nm precision—orders of magnitude better than confocal Raman spectroscopy.

Nanomaterials: The program has used high-resolution superlocalization imaging to reveal the nature and photocatalytic properties of surface reactive sites on single CdS-Au hybrid nanocatalysts. The results from this study bear enormous potential impact on the development of better visible light photocatalysts for solar-to-chemical energy conversion. A simple synthesis for controlled size and

morphology $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbBr}_3$ perovskites was developed. $\text{CH}_3\text{NH}_3\text{PbI}_3$ nanocrystals with several distinct morphologies behave as nonblinking and photostable single particle emitters at room temperature, and may be useful in energy capture devices.

Improving Chemical Separations through Understanding of Weak Interactions

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Funding: \$388,000 (2014)

PROGRAM SCOPE

The goal of this research is to achieve a predictive understanding of the molecular-level interactions in solution that drive the affinity and selectivity between target ions and receptors in chemical separations. Theoretical and experimental efforts will be aimed toward understanding the specific contributions of solvation environment to selectivity in extractive separations. Determining local structure in solution will provide the experimental basis for new understanding of changes in entropy in solvation and binding; molecular-level modeling of solvation and binding interactions will strengthen predictive capabilities for anion extraction; and detailed investigations of the liquid-liquid interface will provide new insights into interfacial effects on extractive separations. To accomplish these specific aims we will take advantage of available and emerging capabilities in neutron scattering and computational sciences at ORNL. Success in this research will enhance the molecular-level predictability of extractive separations, extending the current capabilities from separate quantum mechanical considerations of individual ion-receptor interactions and structural determinations in ordered solids, to a bridging understanding of the important effects of solvent rearrangement on extractive separations. These new capabilities will contribute directly to DOE missions in energy production and utilization, environmental remediation, and to national and energy security.

FY 2014 HIGHLIGHTS

The goal of this program is to develop a general method to measure the hydration structure of aqueous oxyanions using neutron diffraction with isotopic substitution (NDIS) with accompanying classical molecular dynamics (MD) simulations. Previously, the hydration structure of aqueous nitrate ion was confirmed by using nitrogen isotopes, and preliminary data for oxygen isotope substitution was collected. Using MD simulations, a technique to rapidly predict the total scattering for each sample was developed and implemented. It was determined that the difference in scattering signal between the naturally abundant and isotopically enriched samples should be $\sim 0.2\%$, whereas actual measured differences were much larger (3-4%). Once the sources of errors were determined (hydrogen contamination, small concentration differences and sample holder diameter), new methods were developed to remove these prior to the experiment as well mitigate them “on-the-fly” during the course of the experiment. Most hydrogen contamination was eliminated by performing all sample preparation inside a glove box. Small amounts of hydrogen contamination (likely from salts used to create stock solutions), sample thickness and concentration differences were mitigated by titrating with a solution of slightly more concentrated similar concentration and isotopic enrichment, with small amounts of

hydrogen added. This method development effort has significantly paid off, as we just recently made the best measurements of oxygen substituted NDIS we have ever performed. The results show that aqueous nitrate ion does not contain a strong coordination shell of ordered water compared to chloride ion. This is rationalized by the small hydration free energy of nitrate (~300 kJ/mol) compared to e.g., aqueous sulfate ion (~1100 kJ/mol) and that this free energy is spread out over a larger anion compared to chloride (also ~300 kJ/mol). The corresponding MD simulation work on the nitrate system has also been completed.

Spatially Resolved Material Characterization at Interfaces

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Students: 5 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding: \$1,669,000 (2014)

PROGRAM SCOPE

The overarching goal of this research is to surpass the existing analytical capability for nanometer scale spatially resolved material characterization at interfaces under ambient conditions. This is being accomplished through a distinctive merger of advanced spectroscopic and ultrafast time-resolved imaging, scanning probe microscopy, and mass spectrometry. There are two synergistic subtasks in this proposal. In Subtask 1, research is focused on enabling and advancing the ability of ambient surface sampling/ionization mass spectrometry, in combination with other imaging modalities, to study and characterize with submicrometer spatial resolution (100- 1000 nm) molecular and elemental constituents of material interfaces under real world conditions. In Subtask 2, research is focused on utilizing optical spectroscopic methods with high spatial and temporal resolution to provide an understanding of the ultrafast energy flow and chemical reactions in nanostructures and selected functional nanostructure assemblies by imaging individual nanoparticles and nanostructures with chemical contrast, nanoscale spatial resolution, and femtosecond time resolution. Combinations of techniques that capitalize on both optical spectroscopy and mass spectrometry will provide deeper chemical understanding of interfaces than could either discipline alone. Mass spectrometry operates on the molecular level, while our optical techniques probe nanostructures and their assemblies. The new techniques and tools developed under the umbrella of this research proposal to study and characterize a surface, with submicrometer spatial resolution with the ability to specifically identify a wide range of elements, molecular compounds from small molecules to large macromolecules, and functional domains, over a variety of time scales, will be of great utility in the advancement of the DOE mission (including solar energy utilization, energy storage, fuel cells, and catalysis).

FY 2014 HIGHLIGHTS

The mass spectrometry (MS) subtask focused on new concepts for surface sampling/ionization and enhanced material transport and ionization efficiency. A controlled-resonant surface tapping-mode scanning probe electrospray ionization MS imaging platform was shown to provide 35 μm spatial

resolution. It also provided a simple, hands-off means to control the surface to probe liquid microjunction for direct liquid extraction. A transmission geometry laser ablation system combined with a liquid vortex capture probe was implemented for MS imaging enabling a 6 μm spatial resolution. We also advanced a hybrid atmospheric pressure atomic force microscopy/MS imaging system utilizing nano-thermal analysis probes for thermal desorption surface sampling with subsequent atmospheric pressure chemical ionization and mass analysis. The ability to correlate topographic images of a surface and mass spectral chemical images of the same surface, both with nanometer scale resolution was demonstrated. Work within the optical spectroscopy subtask focused on the key electronic excited-state processes in several molecular and polymeric systems, including phlorins, pristine and deuterated P3HTs as well as their thin film blends with PCBM. Extensive effort was taken to develop two femtosecond pump-probe microscopic imaging apparatuses for quantitative assessment of complex electronic excited-state phenomena in spatially heterogeneous systems. The first one is based on an 82 MHz femtosecond oscillator, and its utilization of a white-light continuum probe, offers not only broad spectral range but also can be extended for coherent Raman and electronic four-wave mixing imaging. The second one employs a 250 kHz regenerate amplifier system offers remarkably broader spectral tunability, higher pulse energy and wider applicability than those achievable with the first apparatus. The lower repetition rate makes the second platform particularly suitable for examining long-lived excited state processes.

Solar Photochemistry

Institutions Receiving Grants

Electronically Wired Semiconductor Nanoparticles: Toward Vectoral Electron Transport in Hybrid Materials

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Sr. Investigator(s):
Students: 0 Postdoctoral Fellow(s), 3 Graduate(s), 0 Undergraduate(s)
Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

We are focused on the development of new semiconductor nanomaterials which are prototypical for systems that may be ultimately used to photoelectrochemically produce fuels from sunlight, and in understanding how the introduction of catalytic sites (e.g. metallic tips on a semiconductor nanorod) can alter the band edge energies (E_{VB}/E_{CB}) and the dynamics of electron transfer to/from these nanomaterials

FY 2014 HIGHLIGHTS

We have demonstrated new approaches to a) the characterization of valence band energies using photoemission spectroscopies, which for the first time fully take into account local vacuum level shifts (due to the dipolar nature of the NR), and b) conduction band energies (E_{CB}) using waveguide-based spectroelectrochemical approaches to determine the potentials (versus vacuum) for electron injection into the NC (nanocrystal) or NR (nanorod). Both approaches show significant shifts in band edge energies, and the rates of electron transfer (ET), when NCs and NRs are decorated with metallic and oxide catalytic sites at the NR tip. Even small Au nano-tips on CdSe NRs, where the metallic component is less than 1% of the total atomic content of the NR, introduces shifts in E_{VB} and E_{CB} which are predicted to alter efficiencies of photoelectrochemically driven water splitting and related formation pathways toward solar fuels.

EARLY CAREER: Molecular and Structural Probes of Defect States in Quantum Dots for Solar Photoconversion

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Students: 0 Postdoctoral Fellow(s), 4 Graduate(s), 3 Undergraduate(s)
Funding: \$144,000 (2014)

PROGRAM SCOPE

This project investigates fundamental problems associated with charge photogeneration and transport in emerging solution processed photovoltaic systems. In traditional inorganic semiconductors such as crystalline silicon, the density of charge traps and defects can be reduced sufficiently to permit the electrical transport length to exceed the thickness of material needed to absorb all photons with energy greater than the bandgap of the semiconductor. Emerging solution processed photovoltaic layers composed of organic molecules, colloidal nanocrystals or organo-halide perovskites offer alternate routes to high throughput manufacture that exceed the capacity of crystalline silicon by many orders of magnitude. However, these chemical systems have struggled to achieve defect densities and photochemical stability that are comparable to traditional inorganic semiconductors. In this project, the molecular origins of charge traps and defects are examined in emerging solution processed inorganic systems for solar to electric photoconversion. Charge traps and defects are minority species and so cannot be examined with traditional characterization tools such as X-ray diffraction or electron microscopy that report majority chemical species. Novel infrared electro-optical spectroscopies are developed that permit the introduction of charge carriers into photovoltaic chemical systems that then equilibrate with electronic states at the band edges providing a means to selectively examine charge traps. The infrared spectroscopy permits structurally specific examination of the underlying molecular structures that give rise to these states. The problem of how complex intermolecular interactions in the solid state influence the formation of charge traps and defects is also being investigated by hypothesis based variation of ligand-nanocrystal interactions in colloidal nanocrystals and composition dependent crystallization of organo-halide perovskite photovoltaic systems.

FY 2014 HIGHLIGHTS

This project had earlier demonstrated the ability to tune the density and energetic distribution of charge traps and recombination centers in photovoltaic systems composed of dense arrays of colloidal nanocrystals by systematic variation of ligand-nanocrystal interactions. Collaboration with the Sargent group at University of Toronto revealed that these variations gave rise to a twenty-fold increase in the mobility-lifetime products of the photovoltaic layers with corresponding increases in the solar to electric power conversion efficiencies. One recent effort in this project has focused on overcoming the solubility limitation of ligand exchanged nanocrystals to enable fundamental studies of how ligand-nanocrystal interactions influence the electronic structure and charge transport properties of the systems. This approach involved suspending ligand exchanged nanocrystals in inert polystyrene matrices as a means to prevent inter-particle transport and enable examination of the electronic structure of isolated nanocrystals. Another effort focused on extending the infrared electro-optical spectroscopy techniques to examine molecular species involved in the formation of charge traps and recombination centers in organo-halide perovskite absorbers. Initial work in this direction has used transient infrared spectroscopy to reveal that hydrogen bonded N-H and O-H moieties associated with organic cations in the perovskite phase provide structurally specific probes of the interaction of photogenerated charge carriers with the photovoltaic layer. In future work, this capability will be used to examine the structural origins of charge trapping and photodegradation of organo-halide perovskite systems.

Nano-Structured Electrocatalysts for Conversion of Solar Energy to Fuels

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Principal Investigator: Allen Bard

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Students: 2 Postdoctoral Fellow(s), 2 Graduate(s), 2 Undergraduate(s)
Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

Objectives: We seek advances in the discovery, design, development, fabrication, testing, and fundamental understanding of stable, high-performing, nano-structured materials for solar photoelectrochemical (PEC) production of hydrogen. Practical, sustainable, and scalable solutions will require low-cost, high-availability, stable materials. **Description of the Project:** The project will focus on the discovery and characterization of new nanostructured semiconductor photo-materials and electrocatalysts for PEC systems for production of hydrogen. The morphology of the photo-material is important just as is its compositional make-up; both interactively determine optical and charge-transport characteristics. We will continue and expand the search for new material compositions (including the effects of dopants) and synthesize films of candidate photo-materials for physical and photoelectrochemical characterization. We will also study the performance of amorphous silicon triple junction photovoltaic cells with electrocatalytic and protective coatings. This work is proposed as fundamental research. **Methods:** We will synthesize films of candidate photo-materials by one or more of several synthesis methods, including electrodeposition, chemical spray pyrolysis, drop-casting, reactive ballistic deposition, hydrothermal synthesis, and coatings applied via atomic layer deposition. **Potential Impact:** The development of photocatalytic solar energy conversion as a sustainable, scalable alternative to other forms of energy would provide plentiful renewable energy for the world, whose energy use is projected to double by 2050. As an important chemical feedstock, solar hydrogen could displace at least some production from steam reforming of natural gas, comparatively without emissions of carbon dioxide or sulfur.

FY 2014 HIGHLIGHTS

Over the last year we have conducted several studies of electrocatalysts and nanostructured photomaterials for the production of fuels (especially hydrogen) from solar energy. We have also performed studies of the magnitude and mechanism of electronic conduction in pure and doped bismuth vanadate. This work has resulted in more than one dozen archival journal articles containing the results of these studies. **Future Plans:** We will continue to study Surface Interrogation-Scanning ElectroChemical Microscopy of photomaterials and electrocatalysts searching for photogenerated intermediates. We will also continue to investigate the behavior of semiconductor composites. Finally, we will continue working on the development and characterization of electrocatalysts for both OER and HER and the effect of photomaterial support on electrocatalytic behavior.

Carbon Dioxide Reduction to Organics in an Aqueous Photoelectrochemical Environment: the Impact of Semiconductor Energetics and Aromatic Amine Reaction Dynamics

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Students: 0 Postdoctoral Fellow(s), 4 Graduate(s), 1 Undergraduate(s)
Funding: \$190,000 (2014)

PROGRAM SCOPE

Work during FY 2014 involved the interaction of aromatic amines with p-GaP for the photocatalytic reduction of CO₂ and the synthesis and characterization of new p-type metal oxide semiconductors as photocathodes for the reduction of either CO₂ or H₂O. Mechanistic studies focused on the p-GaP/pyridinium system where a strong dependence on crystal face employed, (111) vs. (100), was detected. We also found a strong potential dependence (formate vs. methanol) on the GaP (100) surface when lutidinium was the catalyst. This finding is contrary to the expected (ideal) behavior of a semiconductor/electrolyte interface and implies a key role for a density of surface states that moderates charge transfer specifically to formate. Separately, we synthesized and characterized the Mg doped delafossite, p-CuFeO₂ and evaluated it as a photocathode for the reduction of CO₂ in aqueous electrolyte. This layered material, has a measured band gap of 1.36 eV with a conduction band edge at 1.1 V vs. SCE. This material selectively reduces CO₂ to formate without the need for a dissolved cocatalyst. Under the conditions we have employed CO₂ is converted to formate at ~800 mV of underpotential. Based on this system we synthesized the analogous delafossite, p-CuRhO₂. We determined a band gap of 1.9 eV. This material was found to be surprisingly inept at reducing CO₂. Rather, it efficiently splits water at zero bias! Further, the material was found to be self-healing at basic pH in the presence of air. Faradaic efficiencies for H₂ production reach 80%, with good electrode stability. This novel system is one of the few photoelectrochemical systems that successfully splits water without external bias under insolation.

FY 2014 HIGHLIGHTS

- Determined that the aromatic amine catalyzed reduction of CO₂ at a p-Gap photocathode has unexpected surface and potential dependences.
- Synthesized a new photocathode material, Mg-doped p-CuFeO₂ and demonstrated the ability of this material to efficiently reduce CO₂ to formate using visible light.
- Synthesized a new photocathode material, p-CuRhO₂ and demonstrated the ability of this material to efficiently split water at zero bias under visible light irradiation.

Semiconductor-Electrocatalyst Contacts: Theory, Experiment, and Applications to Solar Water Photoelectrolysis

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Funding: \$157,000 (2014)

PROGRAM SCOPE

Semiconductor photoelectrodes coated with electrocatalysts are key components of photoelectrochemical (PEC) energy conversion and storage systems. Despite an intense effort aimed at optimizing these materials, there has been little systematic work focused on the semiconductor-electrocatalyst (SC-EC) interface. The SC-EC interface is important because it is responsible for collecting the photoexcited electron-hole pairs generated in the semiconductor. The objectives of this research are to: (1) Understand the rate-/performance-limiting processes at SC-EC interfaces using computer

simulations to predict PEC J-E response as a function of materials parameters. (2) Fabricate and study model systems using single-crystal photoelectrodes to verify predictions and determine how the rates of SC-EC electron/hole transfer and the SC-EC interface energetics vary for different catalyst architectures. The catalyst architectures that will be studied include dense crystalline oxide films, redox-active ion-permeable oxide/hydroxide films, and monolayers of robust inorganic polyoxometalate molecular catalysts. (3) Uncover the interface/catalyst design-principles critical to improving PEC water-splitting photoanodes. This work focused on SC-EC interfaces will therefore fill key knowledge gaps in the understanding of solar-water-splitting using catalyst-modified semiconductor photoelectrodes. This will enable the design of improved materials systems that are practically relevant because they provide a mechanism to directly convert and store solar energy in the form of hydrogen gas, a renewable chemical fuel.

FY 2014 HIGHLIGHTS

We developed a new experimental technique, dual-electrode photoelectrochemistry allowing for direct electrical measurement of the semiconductor-catalyst interface in solar water splitting devices. We also developed the first theory of the semiconductor-catalyst interface and applied the theory through numerical simulation to predict interfacial charge transfer properties of the semiconductor-catalyst junction. We discovered that porous, ion-permeable, redox-active catalysts such as Ni-(Fe) oxyhydroxides form so-called “adaptive” junctions where the effective interfacial barrier height to electron transfer depends on the charge state of the catalyst. This is in sharp contrast to interface properties of dense catalysts, which we found form buried junctions that could be described by simple equivalent electrical circuits. These results elucidated a design principle for catalyzed photoelectrodes - high-performance photoelectrodes with direct semiconductor-catalyst junctions use soft deposition techniques that yield ion-permeable catalysts.

Modular Nanoscale and Biomimetic Assemblies for Photocatalytic Hydrogen Generation

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Richard Eisenberg; Rochester, University of
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Funding: \$240,000 (2014)

PROGRAM SCOPE

The conversion of solar energy into chemically stored energy is a crucial component of efforts to develop solar energy resources in the U.S. and to lessen our dependence on fossil fuels. The primary objective of this project is the development of a multicomponent assembly to convert visible light energy into chemically stored energy in the form of hydrogen (H₂). The proposed photochemical hydrogen production assembly possesses a modular design. The separation of components enables rapid progress through parallel development of individual modules. The three modular components are: 1) a light-absorbing and charge-transfer module consisting of semiconductor quantum dots, 2) a non-porous carbon nanotube membrane that rapidly transfers electrons and protons to a proton-reducing catalyst and separates the light-harvesting and proton-reducing components; and 3) a proton-reducing catalyst in the form of a coordination complex or a metalloprotein that incorporates earth-abundant

metals. Numerous methods are being employed from the fields of biology, chemistry, optics, and materials science and engineering for the development, fabrication, characterization, and testing of the assemblies and their separate components. The experimental methods and techniques required for the project include protein engineering, atomic force microscopy, absorption and fluorescence spectroscopy, time-resolved optical spectroscopy, chemical vapor deposition, optical lithography, current-voltage spectroscopy, synthetic chemistry, electrochemistry, and kinetics studies.

FY 2014 HIGHLIGHTS

A major leap forward in the light-driven generation of H₂ from aqueous protons was taken with the construction of a system in which the light absorber or photosensitizer consists of water-solubilized CdSe quantum dots and the catalyst is an *in situ* formed Ni complex. Activity and robustness are impressive with turnover numbers approaching 1,000,000, activity maintained over 15 days, and a quantum yield for H₂ of 36% with 520-nm light. The activities of a series of catalysts have been assessed with the CdSe photosensitizer. Several specific classes of catalysts were examined including bis-dithiolene complexes of Co and Ni and related derivatives. These complexes possess redox-active ligands that are valuable for assembling two protons and two electrons into H₂ at the catalyst center. A new class of catalysts for H₂ evolution developed consists of artificial hydrogenases based on proteins and porphyrin-peptide assemblies. Electrocatalytic H₂ evolution was accomplished using a water-soluble cobalt porphyrin peptide, CoMP11-Ac, with a turnover number of over 20,000 at nearly quantitative Faradaic yield, at pH 7.0, in the presence of air. Regarding the charge-transfer module, freestanding vertically aligned carbon nanotube membranes have been synthesized and their electron conductivity and proton transport properties characterized. These membranes were used in an integrated system with colloidal CdSe quantum dots to generate photocurrents. The nanotubes were found to have excellent transport properties, directing both electrons and protons over micron distances in a macroscopically directional manner. Materials with these properties are of interest in solar fuel and fuel cell technologies.

Oxomanganese Catalysts for Solar Fuel Production

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Robert Crabtree; Yale University
Charles Schmittenmaer; Yale University
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Funding: \$580,000 (2014)

PROGRAM SCOPE

This project involves close cooperation of our four research groups in the Chemistry Department at Yale University. The goals are to integrate water-splitting catalysts that we have developed with sensitized metal oxide nanoparticles to construct solar-driven photocatalytic cells, and also to investigate how to achieve the advances in efficiency necessary to make photocatalytic water oxidation an economically viable solar fuel resource. In prior work, we have developed new methods for surface attachment of molecular components and catalysts to metal oxide nanoparticles with oxidation-resistant anchors and

linkers that are stable in water and have verified interfacial electron transfer. The specific objectives of the proposed research program are:

- (1) to attach water-oxidation catalysts to mesoporous metal oxide films using anchors,
- (2) to develop photosensitizers that are stable during catalytic turnover, give rapid electron injection upon visible-light excitation, and suppress detrimental recombination while permitting visible light absorption for solar fuel formation,
- (3) to develop structure-activity relationships for charge and energy transfer essential for photocatalysis as characterized by spectroscopic, synthetic and computational methods.
- (4) to couple water-oxidation catalysis to photon-driven single-electron transfer at a photoanode, and
- (5) to couple catalysts for hydrogen production to photochemical water-oxidation in a photoelectrochemical cell.

FY 2014 HIGHLIGHTS

Several new approaches have been developed to attach molecular components and catalysts to metal oxide surfaces and to optimize interfacial electron transfer. By using a modular assembly method, we constructed T-shaped assemblies with a molecular dye bound to a metal oxide surface via an anchoring group attached to pyridine which is axially bound to a high-potential zinc porphyrin. We find that a hydroxamate anchoring group has the best combination of stability and electronic coupling for photoexcited electron injection from a molecular dye into the metal oxide conduction band. We also designed a porphyrin-based model system to examine the use of lateral intermolecular hole transfer as an efficient means to increase transport of holes to a water-oxidation catalyst. Measurement of the hole-hopping kinetics by using transient absorption spectroscopy shows that each hop occurs in 25 ns, enabling efficient hole harvesting for multielectron photoelectrocatalytic applications. In order to enhance the directionality of interfacial electron transfer, we developed a computational screening methodology for systematic search of molecular frameworks with intrinsic electronic rectification. We find that N-phenylbenzamide derivatives are very promising scaffolds to build molecular rectifiers for energy-harvesting purposes.

Graphene Charge Transfer and Chemical Reactions

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

This project focuses on the special electronic and optical properties of graphene with adsorbed molecular species. Graphene makes an excellent substrate for current collection in nanostructured photovoltaic designs. Graphene is almost transparent, and can be used as a solar cell window. It also has no surface states, and thus current is efficiently transported over long distances. Progress in graphene synthesis indicates that there will soon be practical methods for making large pieces of graphene for devices. We now need to understand exactly what happens to both ground state and electronically excited molecules and quantum dots near graphene, if we are going to use them to absorb light in a nano-structured photovoltaic device using graphene to collect photocurrent. We also need to

understand how to shift the graphene Fermi level, to optimize the kinetics of electron transfer to graphene. And we need to learn how to convert local graphene areas to semiconductor structure, to make useful spatially patterned graphenes. In this project we work on several basic science experiments related to these goals.

FY 2014 HIGHLIGHTS

We finished a detailed study of gaseous Br₂ adsorption and charge transfer on graphene, combining *in situ* Raman spectroscopy and density functional theory (DFT).

Radiation and Photochemistry in the Condensed Phase and at Interfaces

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Prashant Kamat; Notre Dame, University of
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Sylwia Ptasinska; Notre Dame, University of
Students: 8 Postdoctoral Fellow(s), 14 Graduate(s), 16 Undergraduate(s)
Funding: \$5,035,000 (2014)

PROGRAM SCOPE

Research at the Notre Dame Radiation Laboratory builds on a long history of significant accomplishment in basic radiation chemistry, impacting fields ranging from nuclear power generation to medical physics, and a world-renowned program in solar energy conversion. A first thrust focuses on homogeneous solutions, often under extreme conditions, integrating both experimental and computational investigations into the physicochemical processes underlying energy deposition and transport in radiolysis and exploring the spectroscopy, structure and reactions of the radicals produced. The second targets radiation processes in heterogeneous environments and tackles the fundamental chemistry of radiation-induced effects at interfaces, probing not only how the interface modifies the radiation chemistry but also how the interface itself is affected. The mechanistic information obtained underpins applications in a wide range of energy and environmental industries. Fundamental radiation science relevant to nuclear energy applications is logically distributed between these two endeavors. Our efforts in solar energy aim to elucidate capture and conversion of light energy by mesoscale architectures, striving to overcome factors currently limiting high overall efficiency. Excited state dynamics in semiconductor quantum dots, carbon nanostructures, and organic semiconductors are probed and new multifunctional hybrid assemblies are identified to optimize photoinduced charge separations. Advances in the biochemical arena employ both ultrafast imaging of charge and energy flow in biosystems and the unique contributions radiation chemistry can make to a detailed understanding of the interaction of ionizing radiation with the components of such systems. This includes radiation damage at synchrotrons during macromolecular crystallography, radiation interactions with biomolecules, particularly the effect of low-energy electrons, and radiolytic oxidation of amino acids, peptides, and alkaloids.

FY 2014 HIGHLIGHTS

Quantum diffusion of atomic hydrogen isotopes was characterized in water using pulse radiolysis/electron paramagnetic resonance over a large temperature range. Deep-UV time-resolved resonance Raman measurements of key inorganic transients in water determined radical structures in solution. Femtosecond transient absorption spectroscopy revealed both long-range Förster and short-range Dexter energy transfer between CdSe quantum dots linked to a squaraine dye and showed mechanistic variation with dot size. Measured excited state dynamics at the band edge of an organo-lead halide perovskite, successfully modeled by Burstein-Moss band filling theory, uncovered promising hole conductor candidates for reaching high efficiencies. Near ambient pressure X-ray photoelectron spectroscopy demonstrated strong water dissociation on a GaAs surface with simultaneous oxygenation and hydroxylation of surface Ga atoms as water pressure increased at room temperature and a growth of As oxides, mainly with rising temperature. The oxidation extent depends strongly on the morphology of the samples. The yields of molecular hydrogen were measured as a function of water loading for irradiated components of resins, widely used for separations and filtering throughout the nuclear industry. A new dissociative electron attachment apparatus provided well-calibrated measurements on isotopically-labeled gas phase N-methylformamide, an initial step toward a better understanding of ionizing radiation effects on amino acids, peptides, and proteins. Thermodynamic thresholds for the observed fragmentations were evaluated using extensive computational quantum chemistry calculations. Optical properties of Frenkel excitons in self-assembled porphyrin tubular aggregates, an analog for natural photosynthetic antennae, were systematically measured by ultrafast optical spectroscopy and modeled by stochastic techniques. Nonradiative pathways induced by traps and defects to dominate the relaxation process.

Low Power Upconversion for Solar Fuels Photochemistry

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Students: 1 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding: \$368,771 (2014-2015)

PROGRAM SCOPE

The original proposal concept related to the development of earth abundant and ideally water soluble/compatible sensitizers and acceptors suitable to drive photochemical upconversion photochemistry in aqueous environments. If successful, upconversion phenomena would be made compatible with solar fuels photochemistry and low energy photons would promote/activate energetically demanding reactions. Initially, this work focused on the development of new classes of photosensitizers incorporating earth abundant metals such as tin and copper to produce Sn(IV) porphyrins and Cu(I) metal-to-ligand charge transfer (MLCT) chromophores, respectively. Similar research lines intend to develop water soluble Ru(II) and Ir(III) MLCT chromophores for possible incorporation as photosensitizers in both upconversion and solar fuels photochemistry. Another related research line seeks to integrate various combinations of donors and acceptors into soft materials enabling photochemical upconversion photochemistry in encapsulated media suspended in aqueous environments.

FY 2014 HIGHLIGHTS

Copper(I) diimine complexes have metal-to-ligand charge transfer (MLCT) absorptive properties similar to $[\text{Ru}(\text{bpy})_3]^{2+}$, without the deactivating ligand field states found in other first row transition metal complexes. However, upon excitation, Cu(I) diimine complexes undergo a significant structural rearrangement, leading to excited states possessing large pseudo-Stokes shifts and very short lifetimes, thereby limiting their usefulness as photosensitizers. Methyl groups in the 3,8-positions of the phenanthroline ligand, combined with bulky sec-butyl groups in the 2,9-positions cooperatively restrict the degree of structural distortion in the Cu(I) MLCT excited state thereby extending its lifetime to the microseconds time scale. This increase in sensitizer lifetime translates to improved performance in sensitized photon upconversion compositions with several anthracene derivatives as triplet acceptors. The newly synthesized cyclometalated coordination compound bathophenanthroline disulfonate-bis-(5-methyl-2-(4-fluoro-phenyl)-pyridine)-iridium(III), displays unique, concentration-dependent photophysics in water, resulting from the formation of complex macromolecular self-assembled structures. The photoluminescence quantum yield and excited state lifetime of this complex markedly increase with increasing chromophore concentration until it achieves a saturation limit. The self-assembly process is clearly evident from simple bubble degassing experiments, which completely remove the chromophores from the aqueous solution in the form of photoluminescent bubbles. Dynamic light scattering experiments suggest the formation of two aggregate structures distinguishable by their hydrodynamic radii. This unique combination of molecular design elements may represent a novel way to control sensitizer structure while enhancing the associated photophysical properties in aqueous media.

Physical Chemistry of Reaction Dynamics in Ionic Liquids

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Claudio Margulis; Iowa, University of
Mark Maroncelli; Pennsylvania State University
James Wishart; Brookhaven National Laboratory
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Funding: \$849,000 (2014)

PROGRAM SCOPE

Ionic liquids are complex fluids that display domain-like structure on the nanometer scale, often exhibiting multiple disordered phases as well as dynamic heterogeneity on the femtosecond to nanosecond time scales. They are emerging as important components in several energy technologies that involve charge transfer and the transport of molecules and charge. This project addresses basic research needs in understanding how emergent aspects of ionic liquids result from individual ion properties and how this knowledge can be used to control transport and charge transfer processes that are important for energy-related applications. This work is part of a five-institution collaboration to achieve a fundamental understanding of charge transfer and transport in ionic liquids, involving the following P.I.s: Blank (Minnesota), Castner (Rutgers), Margulis (Iowa), Maroncelli (Penn State) and Wishart (Brookhaven). Solvated electrons in ionic liquids are studied by ultrafast pulse radiolysis at BNL and transient absorption spectroscopy at Minnesota, together with theoretical work at Iowa.

Mechanisms and dynamics of photo-induced charge separation are studied at Penn State, Rutgers and BNL. Structural studies by the Rutgers group are carried out using synchrotron X-ray experiments at the APS and using 2D-NMR methods. Theoretical studies at Iowa focus on electrons and holes, tracer diffusion of both neutral and charged species, and bulk structural properties of ionic liquids. Work at BNL focuses on pulse radiolysis and flash photolysis studies of diffusion and electron transfer phenomena in ionic liquids, including pressure dependent studies. Another focus at BNL and Rutgers is the design and synthesis of specific ILs for these investigations. The effects of local ionic liquid composition and structure (e.g., the scales of the polar and nonpolar domains within the ionic liquid) on the energetics and dynamics of charge transfer is a particular focus.

FY 2014 HIGHLIGHTS

Theoretical work on ionic liquids (ILs) in the Margulis group progressed on three fronts. Collaborations with the Blank and Wishart groups focused on quantum dynamics of excess electrons and holes in ILs. Experiments in the Blank group concentrated on dynamics of electron detachment, cooling, localization and reactivity in a series of ILs with varying cation sizes, complementing radiolysis studies at BNL by the Wishart group. The Margulis and Maroncelli groups collaborate on understanding mechanisms for neutral vs. charged tracer diffusion in ILs. Margulis group collaborations with the Castner group focused on quantitative comparisons of IL structure from X-ray scattering with molecular simulations. The Castner group complements the X-ray and simulation studies with 2D-NMR studies of specific solute interactions with the IL anions and cations. Time-resolved optical spectroscopy studies of photo-induced charge separation and solvation in ILs have continued in the Maroncelli, Castner and Wishart groups. The Maroncelli group results included studies of solvation and local friction in both neat ILs and in mixtures of ILs with polar solvents such as water and acetonitrile; extensive computer simulations are underway to model the experimental results. Complementary work in the Castner and Wishart groups has focused on both intramolecular and bimolecular photo-induced charge-transfer as a function of cation variation in the ILs. Novel reactive ILs are being used with either anions or cations that serve as electron donors. The Wishart group and collaborators also studied cations with either benzyl- or methylcyclohexyl- moieties, observing that the benzyl-substituted cations have much lower viscosities. The Wishart and Castner groups study reactive N,N-dimethylamino-N'-alkylpyridinium cations that are moderate electron-donors, while cyanate-containing anions are exploited as strong electron donors.

Electrochemical Synthesis of Polycrystalline Semiconductor Electrodes with Optimum Compositions and Morphologies for Use in Solar Fuel Production

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Funding: \$390,000 (2014-2015)

PROGRAM SCOPE

The overall objective of our project is to bring about a marked advancement in the construction, understanding, and available variety of inexpensive polycrystalline semiconductor electrodes for use in solar fuel production by exploiting electrochemical synthesis methods. Electrochemical synthesis can offer a new level of precision and freedom in controlling both the compositions and the interfacial

morphologies of the photoelectrodes. We will establish electrochemical synthesis conditions to produce several highly promising semiconductor systems (e.g. Bi_2S_3 , CuBi_2O_4 , LaFeO_3) with optimum compositions and morphologies to maximize their solar-to-fuel conversion efficiencies. This will significantly broaden our choice of photoelectrodes that can be used to assemble efficient PECs while generating multiple sets of new understanding and insights, which will generally increase our fundamental understanding of semiconductor photoelectrochemistry.

FY 2014 HIGHLIGHTS

We established electrochemical synthesis conditions to produce CuBi_2O_4 as high quality, high surface area electrodes and identified that p-type CuBi_2O_4 is one of the most promising oxide photocathodes. CuBi_2O_4 has a band gap of 1.5-1.8 eV, and, therefore, it can utilize significant portion of visible light. We confirmed that the conduction band edge of CuBi_2O_4 is sufficiently negative to utilize photoexcited electrons for H_2 production. Furthermore, the valence band and flatband potential of CuBi_2O_4 are located at a much more positive potential than those of p-type Si, which is currently considered the most promising photocathode. As a result, it can provide a photovoltage (i.e. the difference between thermodynamic reduction potential of water and photocurrent onset potential) of up to 1.15 V for H_2 evolution. Owing to its early photocurrent onset, CuBi_2O_4 generated a photocurrent density of 1 mA/cm^2 at a potential as positive as 0.8 V vs. RHE. These features make CuBi_2O_4 one of the most promising photocathode systems. We will further improve the efficiency and stability of CuBi_2O_4 for use in solar H_2 production.

Ground and Excited State Structures of Sensitizer Dyes Adsorbed on Semiconductor Nanoparticles

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PROGRAM SCOPE

The Project consists of synthesis of novel polyoxotitanate clusters, crystallization of homodisperse nanoparticles of the new species, measurement of their spectra and electrochemical properties, parallel theoretical calculations. Although a large number of sensitized polyoxotitanate clusters have been reported, detailed information on the electrochemical properties of fully structurally defined nanoparticles and their relation to physical and electronic properties is lacking. Such information is essential for the design of photovoltaic cells of increased efficiency. To address this structure gap we have synthesized a series of transition-metal doped polyoxotitanate nanoparticles, determined their structure and calculated their electronic properties. The clusters prepared include manganese-doped $\text{Ti}_{28}\text{MnO}_{38}(\text{OEt})_{40}\text{H}_2$, $\text{Ti}_{14}\text{MnO}_{16}(\text{OEt})_{28}\text{H}_2$, $[(\text{Ti}_{13}\text{Mn}_4\text{O}_{16}[\text{MeC}(\text{CH}_2\text{O})_3]_4(\text{OEt})_{12}\text{Br}_4)]_\infty$, a series of Ti_{11} cluster of composition $\text{Ti}_{11}(\text{XY})\text{O}_{14}(\text{O}^i\text{Pr})_{17}$ with X= Co, Mn and Fe, and Y= Cl, Br and I. Especially for the Mn and Fe complexes a significant reduction of the bandgap is observed, leading to light-absorption and photo-induced electron injection in the visible region. The work is continuing.

FY 2014 HIGHLIGHTS

Of particular interest are a series of nano particles of which $Ti_{17}O_{28}(O'Pr)_{16}[Fe-phen]_2$ (phenanthroline) (1) and $Ti_{11}(FeBr)O_{14}(O'Pr)_{17}$ are the prototypes. Complex (1) is a member of a doped-functionalized series of nanoclusters in which the phenanthroline is attached to the transition metal atom located on the nanoparticle surface. The visible solution spectrum of the Fe complex (1) shows a series of absorption bands in the 400-900 nm region. Theoretical calculations show the bands in increasing wavelength order to correspond to metal-to-core charge transfer (MCCT), metal-to-ligand charge transfer (MLCT) and d-d metal-atom transitions. Exposure of a thin solid layer of the complex in a photoelectrochemical cell and comparison with theoretical results shows that electron injection in the anode of the cell after photoexcitation occurs from both the titanium oxide particle and from the organic phenanthroline ligand, the latter a result not observed previously. In collaboration with researches at Yale University the femtosecond dynamics of hole injection from the ligand 4-nitrophenyl-acetylacetonate into Ti_{17} nanoparticles was calculated and confirmed by electrochemistry and EPR. The reported experimental and theoretical analysis demonstrates for the first time the feasibility of p-type sensitization of TiO_2 .

Applications to Adaptive Quantum Control to Research Questions in Solar Energy Conversion

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PROGRAM SCOPE

This work explores several photoactive systems at the heart of third generation solar energy conversion strategies. Such strategies aim to increase the upper thermodynamic limit for conversion of sunlight to electrical power or chemical potential. We seek to develop advanced spectroscopic tools and to couple these to new chemical systems as well as modified material systems in order to interrogate fundamental photoconversion processes. A basic understanding of mechanism will permit new molecular or material designs in the future. A primary interrogation tool that is used and developed consists of advanced coherent control spectroscopies such as adaptive pulse shaping. In one area of research we have proposed new tunable bichromophoric molecules supporting singlet fission, to understand the role of specific nuclear motions and electronic coupling pathways for altering photoreactivity and mechanism. Singlet fission is a process by which a single electronic excitation in a molecule or material consisting of coupled chromophoric units is converted to separate electronic excitations on distinct chromophores. With such systems we aim to establish, using adaptive pulse shaping control strategies as well as electronic structure and parameterized theoretical methods, a rigorous understanding of how shaped fields couple to vibrational motions and how these motions perturb electronic properties and affect photoconversion dynamics. These molecules will also allow us make inroads into the development of molecular systems that support singlet fission for eventual utilization in low-cost dye-sensitized or disordered multicomponent thin film solar cells. In a second area of research we aim to consider how thin-film morphology impacts singlet fission yield for polycrystalline tetracene and how a systematic increase of pulse shape complexity affects controllability and illuminates control mechanisms.

FY 2014 HIGHLIGHTS

In 2014 we have been engaged in (a.) synthetic efforts, (b.) troubleshooting ultrafast laser pulse shaping experiments, and (c.) the development of new theoretical/computational tools to quantify molecular electronic properties relevant for singlet fission (SF). In synthesis (a.) we established a working route to generate reasonable quantities of an oxidized dimeric species built via several cyclo-addition and oxidation reactions. With a related model system we identified and optimized conditions for a final reduction step that produces the chromophores of interest. We have put these two facets together and have synthesized the target SF dimer. We have also synthesized a monomeric model system. We are optimizing yields and will then report this and begin photophysical explorations. In the context of pulse-shaping (b.) we have struggled with a loss of control of SF yields in polycrystalline tetracene (Tc) samples that had previously shown response to shaped laser pulses. In searching for root causes we have rebuilt and refined numerous aspects of the general experimental setup and have traced the problem to the pulse-shaper itself and how it impacts the spatial mode of the laser beam. We are currently working with a key part manufacturer to rectify the problem. In collaboration with researchers at NREL we have developed protocols for growth of polycrystalline Tc thin films with control over crystallite size and polymorph type. These efforts are tied to our pulse-shaping control efforts. In our theoretical/computational efforts (c.) we have developed, in collaboration with Subotnik's group at U. Penn, tools for facile determination of SF electronic coupling. These tools are applicable to molecular systems and we have used them to explore the dimer system currently being synthesized. We have explored how molecular vibrations impact this electronic coupling – so called non-Condon effects. This work was published in the Journal of Physical Chemistry A.

Development of Earth-Abundant Transition Metal Catalysts for Water Oxidation

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PROGRAM SCOPE

The current global energy demands for low-cost, clean, and sustainable energy sources have prompted many groups to investigate earth-abundant transition metal complexes as potential catalysts for water oxidation. Our group is investigating complexes with C-F ligand bonds instead of oxidatively susceptible C-H bonds in their scaffold. The chelating bidentate perfluoropinacolate (pinF)²⁻ was proposed as a ligand for air-stable and oxidatively robust complexes that can support highly electrophilic moieties as active species in a water oxidation cycle. This oxygen-donating ligand is virtually unique in the studies of small molecule-based, homogeneous water oxidation catalysts, which generally have nitrogen-donor atoms from the ligands. Oxygen donor systems are particularly important to investigate because the most effective biological and heterogeneous water oxidation systems have metal bound to oxygen. Therefore detailed mechanistic studies to iteratively improve catalysis will be most effective with such a system.

FY 2014 HIGHLIGHTS

Our work has been successful in several important areas: (i) synthesis of a large and flexible family of water-soluble, late transition metal, perfluoropinacolate (pinF) compounds, (ii) structural characterization of five-coordinate water adducts for Co and Ni, (iii) demonstration of homogeneous electrochemical water oxidation catalysis by the $[\text{Co}(\text{OH}_x)(\text{pinF})_2]^{n-}$ system,⁷ (iv) development of new strategy for inhibition of heterogeneous MO_x formation by using the complex ligand as the buffer, (v) comparative spectroscopic and electrochemical studies of the $[\text{Ni}(\text{OH}_x)(\text{pinF})_2]^{n-}$ system, and (vi) discovery of water and nitrate reduction catalysis from $[\text{Cu}(\text{pinF})_2]^{2-}$. The (pinF) chemistry has provided an important framework for studying the mechanism of homogeneous water oxidation catalysis. By investigating this reaction in both the Co and Ni systems, with both experimental and computational work, we now have pH-dependent data that show the important redox energy changes as a function of acidity or basicity. We also have structural data that show how the ligand environment (coordination geometry) changes as a function of oxidation state, including a highly unusual square-planar Co(III) complex from a complementary study in organic media. Our work this past year has been particularly successful in showing a system whose ligand properties of metal chelation are a unique method for the suppression of MO_x formation. Data have shown the pH dependence of precipitate dissolution, consistent with the proposed ligand role. Further studies with Cu species have shown that the pinF system is not only robust to oxidation, but also to reduction. There is great interest to develop systems that are competent in water oxidation and reduction, in a wide pH range to tolerate the protons produced or removed respectively. The demonstration of water reduction with a Cu complex, suggests that the same ligand might be used in both redox processes.

Theoretical Studies of Photoactive Molecular Systems: Electron Transfer, Energy Transport, and Optical Spectroscopy

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PROGRAM SCOPE

This project is aimed at the development of computational methods for modeling solar energy conversion systems, and application of those methods to important solar energy conversion systems. Methods development is currently focused on quantum chemical calculations, specifically density functional theory, with a focus on the determination of redox potentials, pK_a s, energies of different electronic states, spin splittings, and reaction barriers, for organic and transition metal containing systems. The methods development is performed primarily using small organic molecules and organometallic complexes containing a single metal; however, the calculations have to be scaled up to a large cluster model, containing ~300-500 atoms (many of which are transition metals), requiring parallelization of the code in order to get reasonable time to solution. The calculations are performed in continuum solvent (as opposed to vacuum) which is essential in obtaining realistic results for energetics that can be compared with experimental data. The principal application for this granting period has been to understand the functioning of the Gratzel cell, particularly the states relevant to electron

trapping and transport, and the mechanism of hopping transport enabling electrons to move from the site of light excitation to the electrode. Significant progress has been made, as is discussed below.

FY 2014 HIGHLIGHTS

Firstly, we have applied our localized orbital DFT corrections for first row transition metals (DBLOC) to the calculation of pK_a s of hexaquo metal complexes. Standard DFT methods make very serious errors in predicting the pK_a s of these systems, as large as 5-10 pK_a units. Yet the deprotonation of water when attached to a first row transition metal is a key step in catalytic water splitting by such systems. The DBLOC method, employing parameters taken from prior optimization efforts, reduces the average error in our data set from 5.7 pK_a units to 0.9 pK_a units, which is likely close to experimental error. Secondly, we have studied our model for the Gratzel cell under conditions in which hydrogen ions, rather than lithium, are the dominant small ion in the cell solution environment. We find that the hydrogen ions form quasi-covalent bonds with oxygen atoms in the titanium dioxide, leading to greater trap depths and hence higher barriers to electron hopping as compared to lithium. These results are in good agreement with experimental measurements of the trap depth when hydrogen ions are the dominant species, as well as the observed slower rate of electron transport (due to higher activation barriers for electron hopping) under these conditions. Finally, in work as yet unpublished, we have been performing large scale comparisons of our methods with alternative approaches such as the M06-2X density functional, building an anatase (rather than rutile)based model of the titanium dioxide nanoparticle, and are getting ready to model catalytic water splitting reactions at the titanium dioxide surface.

Model Dyes for Study of Electron Transfer Processes at Metal Oxide Semiconductor Interfaces

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PROGRAM SCOPE

The objective of this research program is the design, synthesis, and photophysical study of organic and inorganic chromophore-spacer-anchor model compounds to control and study photoinduced heterogeneous charge transfer processes at the interface between organic chromophores and nanostructured metal oxide semiconductors (TiO_2 and ZnO). We proposed to develop model compounds to study the following: a) the correlation between open circuit photovoltages and charge transfer reactions; b) the influence of a tunable dipole built in the spacer unit on the energy level alignment of the chromophore; c) the mechanisms of iodide oxidation including recombination of injected electrons with oxidized iodide species. To achieve these objectives, we proposed three types of chromophore-spacer-anchor model compounds:

- The synthesis through click-chemistry of a novel class of homoleptic complexes of Ru(II) (Star complexes), that are designed to prevent close contact of the Ru center to the semiconductor by the highly symmetric arrangement of rigid linkers on the ligands.
- The development of rigid-rod chromophores with built-in dipoles in the linker to be aligned parallel or antiparallel to single crystal TiO_2 and ZnO surfaces. Changes in the dipole will shift the molecule

energy level relative to the metal oxide conduction and valence bands, while changes in the functionalization of the chromophore will result in changes primarily in the HOMO-LUMO gap.

- The synthesis and study of N₃-type rigid-rod complexes to understand the factors that control V_{oc} and dye regeneration processes with the Meyer group. The compounds were designed to have enhanced solubility, enhanced light harvesting in the near-IR, and the MLCT excited state localized on a remote bpy ligand.

FY 2014 HIGHLIGHTS

1. Tuning Energy Level Alignment At Organic/Semiconductor Interfaces Using a Built-In Dipole in Chromophore–Bridge–Anchor Compounds S. Rangan, A. Batarseh, K. P. Chitre, A. Kopecky, E. Galoppini, R. A. Bartynski *J. Phys. Chem. C* 2014 118, 12923-12928 DOI: 10.1021/jp502917c
2. Homoleptic “Star” Ru(II) Polypyridyl Complexes: Shielded Chromophores to Study Charge-Transfer at the Sensitizer-TiO₂ Interface P.G. Johansson, Y. Zhang, G.J. Meyer and E. Galoppini, *Inorg. Chem.*, 2013, 52, 7947–7957 DOI: 10.1021/ic4004565
3. Distance Dependent Electron Transfer at TiO₂ Interfaces Sensitized with Phenylene Ethynylene Bridged Ru^{II}-Isothiocyanate Compounds P. G. Johansson, A. Kopecky, E. Galoppini, G. J. Meyer *J. Am. Chem. Soc.*, 2013, 135, 8331–8341. DOI: 10.1021/ja402193f

Monodispersed Design of Zinc-Oxide Nanoparticle-Dye Dyads and Triads

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PROGRAM SCOPE

The primary processes underpinning conversion of light to electrical and/or chemical potential in dye sensitized solar cells comprise a basic competition between the available fates of electrons displaced from equilibrium by the absorption of light. Our continuing development of well-defined dye-metal oxide nanocrystal colloidal dispersions in solution has enabled us to isolate the individual steps of energy conversion and study them in detail. Although the performance of zinc oxide in assembled devices lags that of the more ubiquitous titanium dioxide, the synthetic control of morphology and nanocrystal radius in zinc oxide offers some significant advantages in the current context of detailed, fundamental investigations. When the nanocrystal radii are below ~6 nm, the effects of quantum-confinement alter the band gap and density of states; both of which are expected to play an important role in determining the initial rate of charge injection from the excited state of the attached dyes. From an experimentally important perspective, tight synthetic control over size distributions results in well-defined samples that are optically transparent and easily refreshed. The following projects are being pursued:

- Synthesize new classes of molecular sensitizers that are optimized for charge injection into zinc oxide nanocrystals.
- Investigate the influence of energetic alignment and electronic structure on forward and reverse charge transfer.

- Investigate the influence of the dye binding group and nanocrystal capping chemistry on charge transfer rates.
- Study the dynamics and reactivity of reduced zinc oxide nanocrystals. With dyes bound to their surface, probe the intermediate in the dye sensitization process and evaluate the potential to drive multi-electron chemistry with visible light on such a platform.

FY 2014 HIGHLIGHTS

A comprehensive study of a series of thiophene oligomer based dye sensitizers was completed. The work combined theory and experiment to investigate how tuning the absorption spectrum by extending electronic delocalization via systematic addition of thiophene units influenced charge transfer character and excited state lifetimes. A cyanoacrylic acid group was incorporated for binding to ZnO nanocrystal electron acceptors. Compared to the commonly employed carboxylic acid, the additional electron withdrawing character in the cyanoacrylic acid was successful at maintaining a bias for excited state electron density near the interface even as the size of the oligomer was increased moving the center of mass farther away from the surface. The excited state lifetimes were extended relative to bare thiophenes, and the rate of excited state charge injection into ZnO NCs remained constant with increase in oligomer size. In addition, the binding group was varied on a terthiophene chromophore to quantify its impact on excited state electron transfer rates. Several new inorganic dyes with large excited state reduction potentials (> -1.0 V) were synthesized and their solution surface chemistry with ZnO nanocrystals was investigated. The known compound, $[\text{Bu}_4\text{N}]_4[\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4]$ was synthesized and solution based Stern-Volmer experiments with ZnO nanocrystals showed that the phosphorescence of the longer-lived triplet state was quenched. Three binuclear iridium (I) compounds bearing bridging pyrazolate ligands were synthesized. Each pyrazolate ligand has a carboxylic acid functional group that allowed binding to the ZnO nanocrystals. All complexes displayed both singlet and triplet emission, and Stern-Volmer experiments again established that the triplet state phosphorescence was quenched by ZnO nanocrystals.

Organic Macromolecular Materials for Efficient Transport Properties in Light-Energy Conversion Applications

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PROGRAM SCOPE

Organic materials have great potential for the purpose of inexpensive artificial light-harvesting and energy conversion devices. However, there is still much to be understood regarding the molecular-level mechanisms of solar energy capture and conversion of organic systems in the condensed phase. The focus of this investigation is to probe the fundamental excitation mechanisms in novel organic systems. In this approach, close attention is given to the mechanism and efficiency of a multipath energy transport process in different geometrical organic systems with strong interchromophore coupling. With different steady-state and time-resolved spectroscopic methods as well as with nonlinear microscopy we will characterize the mechanism of energy transport and the relative strength of intra-molecular

interactions in the novel organic macromolecular system. These macromolecules possess unique qualities which might help obtain a better understanding of exciton transport in organic light conversion devices leading to superior efficiencies. The potential impact of this work is the development of a new approach for long range excitation transport and efficient light harvesting in organic macromolecules of different topologies through a deeper understanding of the mechanisms involved in multipath multidimensional energy transport. The experimental methods will be combined with electronic structure calculations as well as phenomenological dynamical calculations. The outcome of the proposed investigations will be a basic understanding and design criteria for long-range excitation harvesting and transport in organic macromolecular systems which will have high impact in the photo-physics, materials chemistry and materials device design areas of solar energy conversion field.

FY 2014 HIGHLIGHTS

New low band gap electron-accepting polymers PNSW, PNTPD, PNPDI and PECN containing thieno[2',3':5',6']pyrido[3,4-g]thieno[3,2-c]isoquinoline-5,11(4H,10H)-dione (TPTI) and fluorine-dicyclopentathiophene dimalononitrile (FDCPT-CN) were investigated. These polymers are based on repeating units of thienothiophene (TT) and benzodithiophene (BDT), and one of the most efficient solar cell materials (PTB-7). The polymers had HOMO levels of -5.73 to -5.15 eV and low bandgaps in the range of 1.47 to 2.45 eV. Fluorescence upconversion studies on the polymers showed longer lifetimes of 1.6 and 2.4 ns for PNSW and PNTPD respectively while PNPDI and PECN showed very fast decays within 353 fs and 110 fs. Two-photon absorption investigation of the polymers showed that the absorption cross sections are in the region of $1.0\text{-}6.4 \times 10^4$ GM per monomer. The electronic structure calculations of the polymers indicated that the LUMO is localized on the electron-withdrawing co-monomers while the HOMO was localized on the more-electron-donating co-monomers. As the difference between the electron affinities of the co-monomers in the polymers decreased, the HOMO and LUMO is more distributed throughout the monomers. Polymers having alternating electron-withdrawing and electron-donating monomers experience enhanced dipole moments necessary for efficient solar cell applications. Also the synthesis of a carbazole bridged porphyrin dimer system which possesses a 90° orientation change between porphyrin units and the single-product four dimer macrocycle, were investigated. Subsequent characterization of the two-photon absorption and ultrafast emission lifetimes of these systems indicates a very strong coupling between constituent dimers in the assembled macrocycle structure. Excitonic coupling through the slipped co-facial arrangement created by imidazolyl-to-zinc interaction was shown to play a critical role in solar cell performance.

Supramolecular Structures for Photochemical Energy Conversion

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PROGRAM SCOPE

Fundamental principles of artificial photosynthesis are being investigated. Artificial photosynthesis is the design, preparation, and study of solar energy conversion systems that are based on the chemistry and

physics of the natural photosynthetic process. Several aspects of the basic science underlying artificial photosynthesis are under study. One involves the design, synthesis, and characterization of new classes of polymers based on porphyrins. These are electrically conducting polymers that absorb visible light and undergo photoinduced electron transfer to generate charge-separated states. They may be useful in new types of solar photovoltaic cells and other optoelectronic applications, in sensors for various purposes, and in molecule-based electronics. A second part of the study involves the fundamental properties of carotenoid polyenes that may be important in artificial photosynthesis. In natural photosynthesis, carotenes act as antenna chromophores and as photoprotective agents. Both functions involve the interactions between carotenoids and cyclic tetrapyrroles such as chlorophyll and porphyrins. Model carotenoid-tetrapyrrole constructs are being synthesized, and their photochemistry is being investigated using transient spectroscopic techniques. These studies are generating fundamental information that is useful in both artificial photosynthesis research and in understanding the functions of carotenoids in natural photosynthesis. Additional investigations involve various aspects of the photochemistry of porphyrins and similar materials that are important for artificial photosynthesis.

FY 2014 HIGHLIGHTS

This year a report was published on the design, preparation and photophysical study of a new soluble, semiconducting porphyrin polymer. This new class of materials may be useful in solar cells for electricity generation, and in other sensing and optoelectronic applications. New dyad molecules consisting of carotenes and phthalocyanines were prepared. Their study revealed unusual electronic (excitonic) interactions between the two chromophores. Additional investigations showed the details of the exchange of both singlet and triplet excitation energy between carotenes and porphyrins or phthalocyanines. These findings will contribute to our understanding of carotenoid antenna and photoprotective functions as seen in natural and artificial photosynthesis. In other studies, we have developed new chemical methods for binding semiconducting polymers and small molecule sensitizers to metal oxides in order to use them in photovoltaic applications. These results showed improved efficiency and stability in investigational solar cells using silatrane-based binding linkages as compared to the more commonly used carboxylates. Finally, complex organic molecules were prepared and sent to collaborators at the National Renewable Energy Laboratory for use in investigations of the fundamental chemistry underlying organic solar cell function.

EARLY CAREER: Molecular and Material Approaches to Overcome Kinetic and Energetic Constraints in Dye-Sensitized Solar Cells

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PROGRAM SCOPE

The general goal of this project is to understand the effect of the dye-sensitized solar cell, DSSC, components – redox shuttle, photoanode, sensitizer, and solvent – on key electron-transfer and electron-transport processes. The interdependent kinetics of these processes – charge injection, dye regeneration, recombination, and charge transport – determine the internal quantum yield of DSSCs.

We are performing a series of systematic investigations of each process as a function of the relevant component in order to develop general structure/function relationships. This knowledge will ultimately allow us to design new molecules and materials capable of overcoming the kinetic and energetic constraints of current generation DSSCs. We are currently primarily interested in understanding the physical underpinning of dye regeneration and recombination reactions. We have synthesized a series of outersphere one-electron redox shuttles with varying potential and reorganization energy to learn what properties of a redox shuttle will allow efficient dye regeneration with minimal driving force and recombination losses. The photoanode material plays a critical role as the electron donor in recombination to both the sensitizer and redox shuttle. A detailed understanding of recombination as a function of material property is therefore vital in choosing a material that is compatible with a given sensitizer / redox shuttle. Another question we are therefore addressing is how the properties of photoanode material, such as surface state density, conduction band energy, and electron mobility, affect the recombination kinetics.

FY 2014 HIGHLIGHTS

We have developed a new spectroelectrochemical method determine the conduction band energy of nanostructured mesoporous semiconductor electrodes by quantifying the Burstein-Moss shift as a function of potential and correlating this with the increased free electron absorbance. We have performed a series of measurements with nanoparticle, NP, TiO₂ in contact with a variety of solvents which allows us to develop a detailed picture of recombination of TiO₂ electrons in terms of Marcus-Theory. In parallel we have synthesized alternative anode materials, including NP SrTiO₃. Work is ongoing to measure the conduction band energy and trap state density of these materials, and measure recombination rates to a series of redox shuttles which will allow us to take an important step of elucidating the details of electron transfer from metal oxide semiconductor NP electrodes and develop general structure-function relationships. In addition, we have performed an extensive series of measurements of the charge collection and regeneration efficiencies of DSSCs employing [Co(ttcn)₂]^{3+/2+} and [Co(bpy)₃]^{3+/2+} redox shuttles in combination with several sensitizers on TiO₂ electrodes, with and without alumina blocking layers. The experiments have consisted of comparisons of the detailed absorption and incident photon to current efficiency, IPCE, measurements from back and front side illumination directions, as well as electrochemical impedance spectroscopy measurements. We have found that [Co(ttcn)₂]²⁺ is capable of quantitative regeneration with minimal driving force loss, while [Co(bpy)₃]²⁺ is not. Recombination to [Co(ttcn)₂]³⁺ limits the diffusion length and thus overall efficiency, which is not the case for [Co(bpy)₃]³⁺ however. Modulation of the recombination kinetics through application of alumina barrier layers offers a method to overcome the differential kinetics. These measurements are now being extended to include the alternative photoanode materials described above.

Solar Energy-Driven Multi-Electron-Transfer Catalysts for Water Splitting: Robust and Carbon-Free Nano-Triads

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Funding: \$308,000 (2014)

PROGRAM SCOPE

The funded project has 5 interlocking fundamental research goals that address core challenges in solar fuel production: (1) Development of oxidatively, thermally and hydrolytically robust, very fast, yet tunable water oxidation catalysts (WOCs). The focus has been on polyoxometalate (POM) WOCs because they are carbon-free, hence oxidatively stable, thermally stable and hydrolytically stable over pH ranges that depend on the metal composition and structure of the POM. Yet unlike metal oxides, they are molecular, thus their structural and electronic properties can be readily studied by spectroscopic, single-crystal diffraction, electroanalytic and computational methods. (2) Chromophore development. (a) New classes of molecular, yet carbon-free photosensitizers (PS) are under investigation, (b) complexes between these PS and POM WOCs are under study. (3) Immobilization of POMs on photoelectrode surfaces. (a) electrostatic, (b) hydrophobic, and (c) covalent immobilization protocols are targeted. (4) Measuring the rates of charge separation and recombination kinetics in our unique multi-component nanostructures. The dynamics in POM-containing dyadic and triadic systems are under investigation. (5) Development of computational methods for POM-based photoelectrocatalysts. (a) A discrete variable representation of an effective mass Hamiltonian has been applied to exciton wavefunctions in quantum confined nanostructures, and (b) hybrid quantum mechanical approaches probe electron transfer in heteronanostructures.

FY 2014 HIGHLIGHTS

This program produced 14 publications over the last year making it as productive as any year for the Emory team thus far.

- 1) Catalyst development. New POM WOCs were designed, in part with computational input, and characterized by spectroscopic, diffraction, electroanalytic and computational methods, including $[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})]^{10-}$, an extraordinarily fast WOC yet one that is very resistant to degradation by air, water and heat. A new class of heterogeneous POM-based WOCs compatible with pH 14 has just been developed (unpublished).
- 2) Chromophore development. The spectroscopic and dynamic properties of a large class of carbon-free (POM) chromophores were characterized. Metal-to-polyoxometalate charge transfer lifetimes were understood as a function of heterometal location within the POM unit.
- 3) Immobilization of POMs on photoelectrode surfaces. Electrostatic methods for POM immobilization were improved and some POM-PS photoelectrodes proved to be very robust. Hydrophobic methods for POM immobilization were improved. An apparatus for collecting meaningful early-time kinetic data in homogeneous catalytic water oxidation with a sacrificial oxidant was reported.
- 4) Measuring the rates of charge separation and recombination kinetics in our nanostructures. The recombination dynamics in irradiated hematite and BiVO_4 semiconductors with and without surface immobilized molecular WOCs have been measured (recent, unpublished work).
- 5) Development of computational methods for POM-based photoelectrocatalysts. An infinite order discrete variable representation of an effective mass Hamiltonian has been applied to exciton wavefunctions in quantum confined nanostructures. Electronic structures of new POM catalysts have been elucidated.

Fundamental Studies of Energy-and Hole/Electron-Transfer in Hydroporphyrin Architectures

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Jonathan Lindsey; North Carolina State University
Christine Kirmaier; Washington University, St. Louis
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Funding: \$620,964 (2014)

PROGRAM SCOPE

The long-term objective of the this highly collaborative research program is to design, synthesize, and characterize tetrapyrrole-based molecular architectures that absorb sunlight, funnel energy, and separate charge with high efficiency and in a manner compatible with current and future solar-energy conversion schemes. The synthetic tetrapyrroles include porphyrins and hydroporphyrins; the latter classes of molecules encompass analogues of the naturally occurring chlorophylls and bacteriochlorophylls (e.g., chlorins, bacteriochlorins, and their derivatives). The studies include (i) gaining a deep understanding of the spectral and electronic properties of bacteriochlorins, especially absorption deeper in the photon rich near-infrared region, (2) achieve panchromatic absorption (broad spectral coverage) while preserving a long, viable long-lived excited singlet state, (3) determination of the rates of ground-state hole/electron transfer between hydro(porphyrins) as a function of electronic and structural design parameters, and (4) construction of integrated architectures that incorporate all the above-noted elements and others to explore the viability of the component parts and processes under application-oriented conditions. The attainment of the goals of the research program requires the close interplay of molecular design and synthesis (Lindsey group), static and time-resolved optical spectroscopic measurements (Holten and Kirmaier group), and electrochemical, electron paramagnetic resonance, resonance Raman, and infrared studies, as well as density functional theory calculations (Bocian group). Collectively, the studies will provide fundamental insights into molecular properties, interactions, and processes relevant to the design of molecular architectures for solar-energy conversion. The accomplishment of these goals is only possible through a highly synergistic program that encompasses molecular design, synthesis, and in-depth characterization.

FY 2014 HIGHLIGHTS

The collaborative research during the reporting period has led to the following advances:

- 1) Synthesis, photophysical and electronic-structural characterization of hydroporphyrins that absorb across the red and near-infrared spectral regions.
- 2) Photophysical and molecular-orbital characterization of panchromatic absorbers that consist of a porphyrin and one to four tightly coupled perylenes.
- 3) Studies of electronic and vibrational properties of hydroporphyrins on surfaces.
- 4) Synthesis and initial characterization of single-unit and multi-component building blocks of an integrated molecular architecture for light-harvesting, energy transfer, and charge separation. Collectively these studies advance our understanding of the design, synthesis and characterization of tetrapyrrole chromophores and arrays for use in molecular architectures for solar energy conversion.

Transition Metal Building Blocks and Assemblies for Photocatalytic Fuel Production

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Funding: \$90,000 (2014)

PROGRAM SCOPE

One of the major scientific and technical challenges of this century is to develop chemical means to store solar energy in the form of fuels. This research program aims to address fundamental questions that underlie the conversion of carbon dioxide to a solar fuel using homogeneous molecular systems. Central to the approaches being pursued is the development of homogeneous systems that catalytically extract the reducing equivalents from dihydrogen, which is a renewable reductant that can be sourced to water, instead of from conventional sacrificial reagents that vitiate solar energy storage. Two main lines of research are being pursued. One effort focuses on understanding the general principles that govern how light-absorbing molecules interact with independent dihydrogen-oxidation and carbon-dioxide-reduction catalysts to produce a functional cycle for driving the energy-storing reverse water-gas-shift reaction with light. The second effort centers on developing the dihydrogen activation chemistry of tungsten–alkylidyne chromophores, which are among the most powerful excited-state reducing agents known and can be incorporated into light-absorbing, catalyst-containing assemblies.

FY 2014 HIGHLIGHTS

We demonstrated that a homogeneous chromophore/two-catalyst system containing hydrogen oxidation and carbon-dioxide reduction precatalysts can be photochemically converted to a catalytically active state, with the energy for this conversion being provided by a low-energy photon. The photochemical mechanism by which this system operates was designed (and found) to be light-induced inter-catalyst electron transfer, as established by transient-absorption spectroscopy. The resulting system is thermodynamically capable of driving the solar-energy-storing reverse water gas shift reaction, and remains in the active state following excitation for sufficient time for the subsequent substrate-transforming steps to take place. It was discovered that the metal-mediated coupling product of carbon dioxide and ethylene is liberated from the metal center through chemical oxidation using bromine, providing functionalized organic anhydrides. This transformation is relevant to the potential catalytic solar-driven production of acrylic acid (a commodity chemical produced on a massive scale) from carbon dioxide and ethylene. A family of tungsten–alkylidyne containing phenylene-ethynylene molecular wires with controllable optical and photophysical properties was designed and characterized. These chromophores contain both a hydrogen-activating center and a linker for connection to carbon-dioxide (and other) reduction catalysts. Analysis of the electronic structures of the compounds as a function of wire length indicated that the degree of electronic coupling between the metal center and the wire could be rationally controlled through variation of the metal and supporting ligands.

Fundamental Studies of Light-induced Charge Transfer, Energy Transfer, and Energy Conversion with Supramolecular Systems

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Funding: \$171,000 (2014)

PROGRAM SCOPE

This project seeks to exploit supramolecular chemistry: a) to interrogate and understand fundamental aspects of light-induced charge transfer and energy transfer, and b) to construct solar energy conversion systems that make use of unique assembly motifs to address key conversion efficiency issues. The project focuses specifically on developing, investigating, and understanding at a fundamental-science level the behavior of promising new light harvesters and redox shuttles in dye-sensitized solar cell (DSC) and DSC-like environments. These new light harvesters include metal-organic frameworks.

FY 2014 HIGHLIGHTS

Given that energy (exciton) migration in natural photosynthesis primarily occurs in highly ordered porphyrin-like pigments (chlorophylls), equally highly ordered porphyrin-based metal-organic frameworks (MOFs) might be expected to exhibit similar behavior, thereby facilitating antenna-like light-harvesting and positioning such materials for use in solar energy conversion schemes. We recently demonstrated that directional, long-distance energy migration, culminating in hole transfer to a molecular partner, can be achieved within an intentionally designed MOF. In FY2014 we showed that: a) hybrid structures comprising MOFs and quantum dots can broaden the spectrum for light harvesting, with the dots serving as antennae for MOFs, b) spatially oriented MOFs, containing multiple light harvesters can be assembled in automated fashion on surfaces with a precision for thickness approaching the dimensions of a single molecular subunit, c) antenna behavior can be observed by appropriately positioning the various chromophores within surface-supported MOFs, d) chromophoric MOFs can be installed on transparent electrodes via the automated synthesis technique, via solvothermal synthesis, and via electrophoretic deposition of pre-assembled MOFs, e) chromophoric sites within these MOFs can be addressed electrochemically, and f) rates of charge hopping between sites, an essential process for conversion of sunlight to electricity via light-absorbing molecules (MOF linkers), can be measured and modulated.

Study of Multiple Exciton Generation with New Multi-Dimensional Spectroscopies

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Funding: \$190,000 (2014)

PROGRAM SCOPE

One approach to high efficiency third generation photovoltaics involves generation of multiple electron-hole pairs (excitons) from a single photon. Novel spectroscopic methods will be developed and applied to probe quantum dot electronic structure, multiple exciton generation, and competing processes in quantum dots synthesized under air-free conditions with controlled surface modifications. Femtosecond two-dimensional Fourier transform spectroscopy will be extended across the short-wave infrared where high efficiency third generation photovoltaics must have their bandgap. We will record two-dimensional spectra to study quantum dot electronic structure and dynamics that have previously been hidden under broad linear absorption lineshapes arising from the distribution of quantum dot sizes. Two-dimensional spectroscopy will also be used to probe the interactions between carriers (electrons and holes) involved in carrier multiplication and the electron-phonon couplings that dissipate energy and compete with carrier multiplication. The Auger recombination process that reverses the beneficial effects of carrier multiplication will be studied using absolutely calibrated pump-probe signals. The overall goal is to determine the carrier multiplication mechanism so that factors influencing the yield can be identified and controlled. More broadly, the novel spectroscopic approaches to be developed and applied here hold great promise as selective probes of the coupling needed for carrier multiplication in third generation photovoltaics. By the end of the project, we aim to develop sufficient mechanistic understanding of the carrier multiplication process in a few semiconductor quantum dots that its potential for third generation photovoltaics can be properly evaluated. The potential impacts include an ability to rationally select quantum dot materials for third generation photovoltaics and non-contact tests for processes that inhibit quantum dot carrier multiplication.

FY 2014 HIGHLIGHTS

We have developed an oxygen free synthesis of lead sulfide quantum dots in the sense that none of the precursors, solvents, or ligands contain oxygen atoms, and all can be rigorously de-oxygenated and dried. The oxygen-free PbS quantum dots have a size distribution comparable to the best obtained in the literature, and their photoluminescence quantum yield is measured at a respectable 30%. We have also developed an ultra-high vacuum level spinning sample cell that is compatible with the interferometric stability required for two-dimensional spectroscopy and allows excitation of a fresh sample for every laser shot. We demonstrated that the oxygen-free quantum dots have a stable absorption spectrum, in solution, for over two weeks of optical experiments inside this new sample cell. We have also developed an exceptionally broadband, actively stabilized interferometer for two-dimensional femtosecond spectroscopy in the short-wave infrared, and extended the bandwidth through interlaced sampling. Two-dimensional femtosecond spectra have been recorded for a number of less-stable lead chalcogenide quantum dot samples (including chlorine passivated dots that are air-stable for months in the solid state, but not stable for more than two days in solution). These two-dimensional spectra reveal the bi-exciton binding energy, which measures coupling between excited carriers, the decoherence time, which measures carrier-phonon coupling, and relaxation times of fine structure normally hidden under the one-dimensional spectrum. We have also measured Auger recombination for hot carrier excitation of 6.2 nm diameter colloidal indium arsenide quantum dots using degenerate transient absorption spectroscopy. The hot bi-exciton signal contains all of the hot single exciton dynamics, plus a new 26 ps timescale attributed to Auger recombination.

Spectroscopy, Photophysics and Charge Transfer Dynamics in Advanced II-VI Semiconductor Nanostructures

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Funding: \$152,000 (2014)

PROGRAM SCOPE

This project focuses on how the composition and morphology of pure and alloyed II-VI semiconductor heterostructures control their spectroscopic and dynamical properties. This research uses a combination of synthesis development, electron microscopy, time-resolved electronic spectroscopy and modeling calculations to study these nanostructures, and examines the extent to which morphology, compression due to lattice mismatch and alloy effects can be used to tune the electron and hole energies and the spectroscopic properties of II-VI heterojunctions. It also uses synthesis, optical spectroscopy and HRTEM to examine the role of lattice mismatch and hence lattice strain in producing interfacial defects, and the extent to which defect formation can be prevented by controlling the composition profile through the particles and across the interfaces. In addition, the project involves the study the magnitude of the surface roughness in core/shell nanostructures and the role of shell thickness variability on the inhomogeneity of interfacial charge transfer rates.

FY 2014 HIGHLIGHTS

We have recently published experimental results and computational model calculations that lead to a few very simple conclusions about the morphology of CdSe/CdS core/shell quantum dots. We have shown that smooth shell growth is thermodynamically favored during the initial deposition of CdS shell on a CdSe core. As shell deposition proceeds the lattice strain energy increases. At some point, depending on the core size and shell thickness, the strain energy density becomes sufficiently great (27 eV or 0.59 eV/nm^2) that the shell undergoes reconstruction to a higher surface area, lower strain morphology. This typically creates defects and thereby lowers the luminescence QY. Shell reconstruction is an activated process and if the shell is deposited at a sufficiently low temperature, much higher strain energies will be obtained before the shell undergoes reconstruction. This is desirable for making well passivated, highly luminescent CdSe/CdS particles.

Next-Generation Semiconductors for Solar Photoelectrolysis

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Students: 0 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding: \$141,000 (2014)

PROGRAM SCOPE

The objective of this research is to gain a better understanding of the chemical and physical processes occurring at the surface of and within the bulk of pyrochlore family semiconductor oxides, enabling the design of systems with high quantum efficiencies for visible-light-driven solar water splitting. Pyrochlore family semiconductor oxides provide an active, robust, and tunable direct band gap semiconductors with band gaps between 2 and 4 eV that can be used to understand and eliminate the barriers to efficient visible light water splitting. The novel thin film and single crystal growths of some complex oxide pyrochlore phases which show promise for visible light water splitting will be carried out. These samples will be characterized to obtain accurate measurements of their light absorption and their electronic conduction, providing the insights required to improve their ability to harvest the energy of sunlight to produce hydrogen fuel.

Water splitting chemical reactions occur at a surface, either of the semiconductor or of an attached co-catalyst, and specific chemical sites participate in this reaction. The single crystal and epitaxial film pyrochlore family semiconductor surfaces will allow surface species to be probed by a wide variety of surface science techniques, offering insights into chemical reaction mechanisms and chemical intermediates through these collaborative experiments. Both direct and collaborative studies will be done of semiconductor surface structure. Electrochemical and photoelectrochemical methods will be used to evaluate the efficiency of these materials for carrying out water splitting reactions.

FY 2014 HIGHLIGHTS

No FY14 Highlights provided.

Establishing the Role of the Electrode Surface in Solar-Driven Pyridine-Catalyzed CO₂ Reduction

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Funding: \$615,000 (2014-2016)

PROGRAM SCOPE

This research applies to the generation of chemical fuels by solar-driven CO₂ reduction. Our work studies catalysts that can be used to efficiently carry out this process, with a goal of increasing both the rate and selectivity of fuel production. In particular, we are investigating the pyridine (C₅H₅N) catalyzed conversion of CO₂ to methanol, which when used in a photoelectrochemical cell employing a p-type gallium phosphide (GaP) photocathode, is the most efficient recorded photoelectrocatalytic system for methanol fuel generation. However, despite considerable electrochemical characterization and theoretical consideration, there is currently no consensus on the mechanism by which pyridine catalyzes CO₂-to-methanol conversion, and this limits the pace of continued optimization of catalysts for solar-driven CO₂ reduction. In our research, we use a surface science approach to establish a molecular-level understanding of the reaction mechanism and specifically probe the role of the semiconductor electrode surface in pyridine-catalyzed CO₂ reduction. We will characterize the atomic and electronic structure of GaP single crystal surfaces, beginning with studies of GaP(110), and identify active sites for reactions with hydrogen, water, and pyridine using a powerful array of surface analytical tools. This will answer

basic questions regarding the structure of these adsorbates on the surface, as well as provide a foundation for the more complex chemistry studied subsequently. Surface-bound intermediates, as well as their thermal stabilities in the dark and illuminated conditions, will be characterized. Their reaction with CO₂ and other compounds along the CO₂-to-methanol pathway, including formic acid and formaldehyde, on the GaP surface will be investigated to develop a fundamental framework for understanding this catalysis and advancing catalyst development.

FY 2014 HIGHLIGHTS

Our initial experiments involved high-resolution electron energy loss spectroscopy (HREELS) and high-resolution X-ray photoelectron spectroscopy (XPS) and ambient pressure photoelectron spectroscopy (AP-PES) studies to characterize GaP(110) and the interaction of H₂O and pyridine with the GaP(110) surface. We observed a partially dissociated water layer consisting of adsorbed H₂O and surface-bound OH and H species. Current work is exploring the role of these species in the mechanism of CO₂ electroreduction. Pyridine is molecularly adsorbed and interacts with GaP(110) via a dative bond between the N lone pair and surface Ga atoms. These baseline measurements provide a foundation for the more complex chemistry that we are presently investigating. Future studies will entail low-temperature STM studies of the adsorption sites and geometries of pyridine and CO₂ on GaP(110) and *in situ* measurements of ultrafast transient spectroscopy, which probes carrier dynamics during charge transfer to adsorbates involved in CO₂ reduction. We have also established collaboration with E. A. Carter's group at Princeton to provide theoretical insights for our experiments. Their DFT calculations explore adsorption configurations of a partially dissociated layer of H₂O on GaP(110) and adsorption sites and molecular geometries of relevant molecular catalysts on GaP(110).

Photophysics & Photoinduced Charge Transport in Single Walled Carbon Nanotubes

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Funding: \$129,000 (2014)

PROGRAM SCOPE

This proposal addresses the general use of novel nanometer scale materials to solve fundamental impediments to further developing cheap and efficient solar energy through studies of the photophysical and photoinduced charge transport properties of single walled carbon nanotubes. For example, more efficient solar cells based on carbon nanotubes, which would be inexpensive, could lower overall solar energy costs such that they can potentially compete with the costs of energy from carbon-based fuels. These proposed studies will result in a deep understanding of the fundamental optical physics of this novel nanoscale material, and perhaps may lead to the development of new technologies based on nanotube photonics. For example, carbon nanotubes are attractive materials for potential use as efficient nanometer scale energy conduits, since they are able to transport charge long distances with minimal energy loss. In this project time-integrated and time-resolved photoluminescence from long nanotubes under electrochemical control will be used to better characterize and thus further understand the photophysics of single walled carbon nanotubes. In particular, these spectroelectrochemistry studies will be used to obtain the reduction and oxidation

potential of individual nanotubes, unknown at present. In a second project, ultrafast pulses will be used to generate (and detect) many electron-hole pairs in single-walled carbon nanotubes through single photon multiple exciton generation processes. The generation of more than one electron-hole pair (i.e. exciton) from a single photon is a simple way to enhance solar cell conversion efficiencies since in this process excess electron and hole kinetic energy is converted into another electron-hole pair. The fate of those multiple excitons is also very important and will be a focus of this project.

FY 2014 HIGHLIGHTS

Using spectroelectrochemistry on the single nanotube (NT) level we found the photoluminescence (PL) of individual NTs was quenched at positive and negative potentials, as electrons or holes filled the conduction or valence band energy levels, respectively. However, the onset of the PL quenching varied significantly from NT to NT, by upwards of hundreds of meV. Thus, we concluded that the same type of NT can have reduction or oxidation potentials that vary by hundreds of meV depending on its surroundings. We proposed that differences in the local environment of the individual NTs lead to a shift of the Fermi energy, resulting in a distribution of the oxidation and reduction potentials. It is currently not understood why NTs have PL quantum efficiencies that are at best a few percent. To get a deeper understanding of NT PL we studied PL from NTs wrapped in derivatives of polyfluorene polymers (PFOs) at temperatures between 77 and 300 K. We have focused on a sideband in the PL spectrum about 140 meV to the red of the main excitonic PL peak due to a photon mediated transition (called the K-momentum dark exciton or KDE peak). The coupling of a phonon to the nominally “dark” exciton transition was thought to take place through emission of a D-band phonon, but these conclusions were drawn from studies that were only on a single chiral NT species (i.e. (6,5) NTs only). We have found that the KDE peak actually disappears at low temperature, suggesting that the KDE transition involves absorption and not emission of phonons, and we are formulating a theory of the involvement of phonons in NT PL consistent with our observations. We also set up a single molecule confocal microscope that can operate at low temperatures down to 4 K. We have begun experiments to use single molecule spectroscopy at temperatures between 10 and 300 K to better understand the nature of the trion emission from NTs, and thus important charged particle interactions in NTs.

Light-Driven Charge Separation in Face-To-Face Donor-Spacer-Acceptor Supramolecular Systems

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Funding: \$360,000 (2014-2015)

PROGRAM SCOPE

Optimization of the efficiency of photoinduced charge separation provides one of the fundamental challenges to the utilization of solar energy. The DNA conjugates developed in our laboratory provide versatile model systems for the study of the basic processes which determine the efficiency of multistep photoinduced charge separation and for the optimization of this process. The chronology of photoinduced charge separation in DNA hairpins modified with electron acceptor chromophores can be divided into three stages. In the first stage, which occurs within the first few ps, an exciplex or radical ion pair involving the chromophore and adjacent base pair is formed either via excitation of the

chromophore followed by charge transfer or direct excitation of a charge-transfer transition. Following this initial stage, spatial separation of the radical ion pair occurs on the ps-ns time scale to yield a charge-separated radical ion pair. Finally, the hole on the base pairs can migrate via an incoherent random walk until it reaches a trap site. Whereas the overall process can be described in broad outline, the details of the two initial stages remain incompletely understood in the case of hole (positive charge) transport and largely uninvestigated in the case of electron transport. It is the objective of this project to investigate several specific aspects of the charge separation process in DNA. The effect of driving force and the separation of the chromophore and base pair by an insulating cyclohexane-derived base pair on the initial charge separation process will be investigated. Special attention will be paid to the injection and transport of electrons in novel donor-bridge-acceptor systems designed for this application. The effect of cation radical or anion radical confinement on a finite number of identical bases will also be investigated.

FY 2014 HIGHLIGHTS

Several organic chromophores as electron acceptors or donors have been investigated in studies of DNA electron transport during FY 2014. 4,4'-Dimethylaminobenzophenone (Michler's ketone) is best known as a triplet sensitizer, but can also serve as an electron acceptor or donor by virtue of the charge-transfer character of its excited state. Hairpins possessing a Michler's ketone linker undergo fast singlet state charge separation and charge recombination with an adjacent purine base, attributed to well-stacked ground state conformations, and intersystem crossing to the triplet state, attributed to poorly-stacked ground state conformations. The failure of the triplet to undergo electron transfer reactions on the 7 ns time scale of our measurements is attributed to the low triplet energy and reduction potential of the twisted triplet state. Naphthalenediimide (NDI) is a powerful singlet state electron acceptor. Both the initial charge injection and subsequent charge separation processes for NDI hairpins are more rapid than those for hairpins with linkers that are weaker acceptors such as stilbenedicarboxamide (SA) or PDI. In addition to investigating the driving force dependence of the dynamics of charge separation, we are also investigating the effect of inserting a pair of cyclohexane (CX) base analogs between the chromophores and first A-T or G-C base pair. The CX base pair serves as a tunneling barrier for hole injection. 4,4'-Dialkoxystilbenes are strong electron donors capable of injecting electrons into adjacent pyrimidine bases. We have recently completed an investigation of the dynamics of electron injection and charge recombination for natural purines and several halogenated purines and find that T₁Un sequences (FU = 5-fluorouracil) provide the highest yields and longest lifetimes for the formation of charge separated states.

Investigations of the Fundamental Interfacial Chemistry and Physics of Functionalized Zn₃P₂, WS₂, and Partially Metalized Semiconductor Surfaces

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Funding: \$209,000 (2014)

PROGRAM SCOPE

This project focuses on developing an understanding of, and control over, the behavior at interfaces between semiconductors and liquid electrolytes in photoelectrochemical systems that convert solar energy to either electricity or fuels. The behavior of photoelectrochemical systems depends on an interplay between often competing factors, including the morphology, surface-state density, interfacial charge transport, and electrocatalytic properties of semiconductor/liquid interfaces. In this project, an understanding of these factors is being developed through fundamental studies of the surface and interfacial phenomena of promising non-traditional semiconductor systems, such as transition-metal chalcogenides, and through studies of electron-transfer and charge-equilibration processes of traditional semiconductors in contact with discontinuous phases with distinct interfacial chemistries. The goal of this work is to increase the viability of the studied systems for use in photoelectrochemical energy-conversion devices and to guide future explorations and improvements into the surface properties of other non-traditional semiconductors.

FY 2014 HIGHLIGHTS

Layered transition-metal chalcogenides, such as molybdenum disulfide and tungsten diselenide, are attractive non-traditional semiconductors for use in solar energy-conversion devices. The crystal structures of these materials consist of layers – each layer consisting of a sheet of metal atoms between two sheets of chalcogen atoms, with adjacent layers held together by van der Waals interactions. The surface of the crystals is characterized by chemically stable chalcogen-terminated terraces terminated by edge sites which provide a pathway for degradation and performance losses. We have synthesized crystals of p-type tungsten diselenide by chemical-vapor transport and fabricated photocathodes from the crystals. *In situ* laser-beam-induced current (LBIC) microscopy was used to map the photocurrent produced by illuminated photocathodes in contact with an aqueous solution containing a fast, one-electron redox couple. We also applied the LBIC technique to studies of photocathodes in contact with sulfuric acid, with and without platinum deposited on the surface. For the case of bare tungsten diselenide photocathodes, we found that edge sites correlate with a decrease in photocurrent, supporting the hypothesis that edges act as carrier-recombination centers. However, we also found that different terraces can have significantly different photoactivity, and that the presence of low-performing terraces may be more detrimental to the performance of a device than macroscopic edges. For the case of photocathodes in acid under conditions of hydrogen evolution, the *in situ* LBIC study and a post-measurement scanning electron microscopy (SEM) analysis showed that areas of high photoconversion efficiencies directly correlated with the presence of the platinum catalyst in those areas. These studies have provided a detailed picture of the photoconversion processes on transition-metal chalcogenide electrodes.

Colloidal Type II Nanorod Based Triad/Antenna Complexes for Solar-Fuel Conversion

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Funding: \$184,146 (2014)

PROGRAM SCOPE

The long-term goal of the proposed project is to prepare and investigate novel colloidal semiconductor nanostructure assemblies for efficient solar-to-fuel conversion. These assemblies, consisting of light harvesting antennas and charge separation triads, are capable of efficient photon absorption, charge separation, charge accumulation, and catalysis under solar flux. The colloidal inorganic triads, based on epitaxially grown type II hetero-nanorods (NR) with attached hydrogen evolution catalysts (such as CdSe-CdS-Pt), have built-in directional charge separation and tunable optical, electronic and catalytic properties. The design and improvement of such photocatalytic triad/ antenna complexes requires a fundamental understanding of the photophysics and charge transfer properties of the NR triads. The first objective of the proposed plan is to investigate single and multiple exciton relaxation as well as single and multiple charge separation and recombination dynamics in NR based dyads and triads by transient absorption spectroscopy. The initial studies are focused on CdSe-CdS and CdSe-CdS-Pt quasi-type II NR dyads and triads and related materials, examining how exciton relaxation and charge separation properties depend on the constituent materials and their dimensions. In addition to guiding the design and optimization of these materials, the proposed study will also provide a fundamental understanding of whether and how the one-dimensional (1-D) excitonic structures in the NRs affect their exciton relaxation and dissociation dynamics compared to the much better understood 0-D excitons in quantum dots (QDs). The second objective of the proposed plan is to investigate the interaction mechanism between plasmons in the metal tip with the semiconductor domain in semiconductor-metal heterostructures. Using CdS-Au and CdSe-Au as model systems, this study investigates the key parameters that control the efficiency of plasmon induced hot electron transfer.

FY 2014 HIGHLIGHTS

We completed three projects from Oct 1, 2013 to September 30, 2014. 1) Auger-assisted electron transfer from Quantum dots. In an effort to test theoretical models for describing ET from excitonic nanomaterials, we investigated electron transfer in QD-molecular complexes. We showed that the rate of photoinduced electron transfer from QDs to molecular acceptors increased at increasing driving force. We accounted for this unusual driving force dependence by proposing an Auger-assisted electron transfer model, in which the transfer of the electron can be coupled to the excitation of the hole. Because Auger-type processes occur in most quantum confined nanomaterials, we believe that the Auger assisted ET model should be generally applicable for describing exciton dissociation in other nanomaterials. 2) Plasmon induced hot electron transfer in CdS-Au nanorods. In this paper, we demonstrate that the optical excitation of either the Au tip and CdS NR can lead to charge separation across the semiconductor-metal interface. This finding suggests the possibility of further optimization of plasmon induced hot electron injection efficiency through controlling the size and shape of the plasmonic and excitonic domains for potential light harvesting applications. 3) Hole removal limits H₂ generation quantum efficiency in CdSe-CdS-Pt and CdS-Pt nanorods. Semiconductor-metal nano-heterostructures are promising materials for solar-to-fuel conversion because they allow rational integration of an light absorber, hole acceptor, and electron acceptor or catalyst in an all-inorganic triadic heterostructure. To provide design principles of such triadic nanorods, we examined the photocatalytic H₂ generation quantum efficiency and the rates of elementary charge separation and recombination steps of CdSe/CdS-Pt and CdS-Pt nanorods. We showed that hole transfer is a key efficiency-limiting step.

Fundamental Studies of Energy- and Hole/Electron-Transfer in Hydroporphyrin Architectures

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

The long-term objective of the this highly collaborative research program is to design, synthesize, and characterize tetrapyrrole-based molecular architectures that absorb sunlight, funnel energy, and separate charge with high efficiency and in a manner compatible with current and future solar-energy conversion schemes. The synthetic tetrapyrroles include porphyrins and hydroporphyrins; the latter classes of molecules encompass analogues of the naturally occurring chlorophylls and bacteriochlorophylls (e.g., chlorins, bacteriochlorins, and their derivatives). The studies include (i) gaining a deep understanding of the spectral and electronic properties of bacteriochlorins, especially absorption deeper in the photon rich near-infrared region, (2) achieve panchromatic absorption (broad spectral coverage) while preserving a long, viable long-lived excited singlet state, (3) determination of the rates of ground-state hole/electron transfer between hydro(porphyrins) as a function of electronic and structural design parameters, and (4) construction of integrated architectures that incorporate all the above-noted elements and others to explore the viability of the component parts and processes under application-oriented conditions. The attainment of the goals of the research program requires the close interplay of molecular design and synthesis (Lindsey group), static and time-resolved optical spectroscopic measurements (Holten and Kirmaier group), and electrochemical, electron paramagnetic resonance, resonance Raman, and infrared studies, as well as density functional theory calculations (Bocian group). Collectively, the studies will provide fundamental insights into molecular properties, interactions, and processes relevant to the design of molecular architectures for solar-energy conversion. The accomplishment of these goals is only possible through a highly synergistic program that encompasses molecular design, synthesis, and in-depth characterization.

FY 2014 HIGHLIGHTS

The collaborative research during the reporting period has led to the following advances: (1) Synthesis, photophysical and electronic-structural characterization of hydroporphyrins that absorb across the red and near-infrared spectral regions. (2) Photophysical and molecular-orbital characterization of panchromatic absorbers that consist of a porphyrin and one to four tightly coupled perylenes. (3) Studies of electronic and vibrational properties of hydroporphyrins on surfaces. (4) Synthesis and initial characterization of single-unit and multi-component building blocks of an integrated molecular architecture for light-harvesting, energy transfer, and charge separation. Collectively these studies advance our understanding of the design, synthesis and characterization of tetrapyrrole chromophores and arrays for use in molecular architectures for solar energy conversion.

Electron/Hole Selectivity in Organic Semiconductors for Solar Energy Conversion

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Funding: \$332,000 (2014-2015)

PROGRAM SCOPE

The selective collection of charge carriers (electrons or holes) is a critical step in the direct conversion of light into electricity. Organic semiconductors (OSCs) are being widely explored as selective contacts to both organic and inorganic absorber materials in the development of high-efficiency photovoltaics, but the fundamental mechanisms underlying selectivity are not fully understood. The goal of the proposed program is to quantify the electron/hole selectivity of OSC contacts and understand the fundamental origin of this selectivity in terms of relevant microscopic rate processes. The approach involves the study of a range of organic semiconductors using (1) a model system specially designed to probe electron/hole selectivity, (2) comparison of the results from this platform to the energy conversion properties of photovoltaics based on common absorbers where OSCs are finding application, and (3) the introduction of junction transient photocapacitance and photocurrent measurements to directly measure the relative efficiency of electron versus hole collection of complete photovoltaic systems.

FY 2014 HIGHLIGHTS

During the first 90 days of the project, we successfully developed and demonstrated the utility of the proposed platform for studying selectivity and developed the necessary numerical modeling tools for interpreting the results.

EARLY CAREER: Bio-Inspired Electro-Photonic Structure for Dye-Sensitized Solar Cells

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Funding: \$160,000 (2014)

PROGRAM SCOPE

Efficient absorption of photons and effective carrier extraction are usually antithetical goals in traditional photovoltaic device configurations. Typical solar cell designs try to maximize photon capture by increasing the thickness of the absorbing layer. But this is detrimental to charge harvesting since increased transport path lengths lead to increased carrier recombination. The objective of our program is to comprehensively redesign the full opto-electronic properties of dye sensitized solar cells to develop the ultimate cell structure, at all length scales, which will enable DSSCs with perfect light capturing and electron harvesting. Our program is based on two developments advanced by our laboratory that decouple carrier transport from optical absorption: 1) A novel high surface area oxide fabrication technique "corn-field" that significantly improves anode properties over conventional nanoparticle sintering. This is especially relevant since this unique photo-anode nanostructure allow us to use thinner films to achieve full dye loading and at the same time provide more direct paths for charge transport, reducing travel lengths and recombination opportunities. 2) The optical control allowed by non-invasive

photonic structuring in solar cells. In contrast to conventional planar cell designs or bulky inverse opal photonic crystal approaches that degrade the electronic performance, a photonic crystal design can provide optical enhancement to the wavelengths where it can be most beneficial (the red side of the absorption spectrum where material's absorption is the weakest) and also reduce electrical transport lengths requirements simultaneously. Together this two independent technologies will allows us great latitude to understand and ultimately control in the optoelectronic properties of the dye sensitized photoanodes.

FY 2014 HIGHLIGHTS

Porous $\text{In}_2\text{O}_3:\text{Sn}$ (ITO) films resembling from brush carpets to open moss-like discrete nanostructures were grown by pulsed laser deposition under low to high background gas pressures, respectively. The charge transport properties of these nanoporous substrates were probed by pulsed laser photo-current and voltage transient measurements in N719 dye sensitized devices. Although cyclic voltammetry and dye adsorption measurements suggest a lower proportion of electro-active dye molecules for films deposited at the high-end background gas pressures, the transient measurements indicate similar electron transport rates within the films. Solar cell operation was achieved by the deposition of a conformal TiO_2 shell layer by atomic layer deposition (ALD). Much of the device improvement is shown to be due to the TiO_2 shell blocking recombination of photoelectrons with the electrolyte as recombination lifetimes increased drastically from few seconds in uncoated ITO to over 50 minutes in the ITO with TiO_2 shell layer. Additionally, an order of magnitude increase in the electron transport rate in ITO/ TiO_2 (core/shell) films was observed, giving the core-shell structure a superior ratio of recombination/transport times. We have also started to probe the potential use of our nanostructure photoanodes for other types of devices beyond the DSSC. In particular, we have analyzed with full computational optoelectronic design their applicability with Quantum dot solar cells. With simple photonic nano-structuring, we can show potential improvements from 8 to 16% efficiency improvements that we will try to realize in the coming year.

Light-Stimulated Hole Injection at Dye-Sensitized Phosphide Photocathodes

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Funding: \$133,000 (2014)

PROGRAM SCOPE

The primary research objective of this proposal is to measure hole injection from a photoexcited, adsorbed sensitizer into an inorganic semiconductor photoelectrode, with the impetuses to develop a more detailed, quantitative understanding of dye-sensitized systems and to construct efficient dye-sensitized photo-electrodes for solar energy storage and conversion using phosphide semiconductors. Light-stimulated hole injection is of immense importance for solar energy applications for two reasons. First, sensitized hole injection is the inverse of the sensitized electron injection process used successfully in 'Grätzel' cells. Second, dye-sensitized hole injection is naturally compatible with using optical energy to drive reductions that result in energy-rich chemical fuels. The regenerative redox couple can be reduced by the dye and can either be directly coupled to pertinent electrochemical transformations, e.g.

reduction of H^+ or CO_2 , or be the desired redox reactions themselves. Despite early experimental evidence showing that both light-stimulated electron and hole injection in dye-sensitized systems are possible, the primary focus of most research groups has been on photoexcited electron transfer processes. As a result, while the capacity for solar energy conversion of electron-injection-based dye-sensitized n-type semiconductor electrodes has advanced significantly over the past four decades from the level of lab curiosity to commercially viable photovoltaic architectures, the development of dye-sensitized p-type photoelectrodes is still in its infancy.

FY 2014 HIGHLIGHTS

In the third full year of funding, we made progress on several important aspects of the project. First, we showed a viable surface functionalization route for p-GaP photoelectrodes through the reaction between surficial P-O-H groups and alkyl/ benzyl bromides via a Williamson ether-type synthesis. Surface analyses (i.e. FTIR and XP spectroscopies) indicated the introduction of a disordered monolayer of alkyl chains through an ether-like P-O-C linkage. Surface reaction yields were tightly regulated through the action of a nucleophilic base promoter, highlighting a level of control atypical of analogous reaction chemistries on pure metal oxide surfaces. The collected evidence supported the premise that the resultant surface state density is low enough to support sensitization with high internal quantum yield if the extent of depletion/ inversion in the p-GaP photoelectrode is sufficient. Second, we demonstrated that GaP surfaces reacted with CH_3MgCl showed markedly enhanced chemical stability with respect to cathodic degradation. Although cathodic operation is generally perceived to be less corrosive towards semiconductor photoelectrodes in water, reductive degradation of binary p-type semiconductors through the formation of metallic clusters/particles is possible. Specifically, since native GaP surfaces are not electrocatalytic towards H^+ reduction in water, photogenerated electrons in p-GaP that reach the electrode/electrolyte interface may participate in the reduction of atop Ga atoms which form metallic Ga clusters/particles. Depending on the Pourbaix diagram of the electrolyte, the newly formed elemental Ga either can leach into solution (e.g. in $NaOH$, H_2SO_4) or accumulate on the surface (H_3PO_4). Either scenario results in a catastrophic attenuation/elimination of photocurrent. Following 15 hours of illumination and net cathodic current passage, the CH_3 -terminated GaP(111)A electrodes retained 66% of the photocurrent passed at $t = 0$.

Nanostructured Photocatalytic Water Splitting Systems

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Funding: \$190,000 (2014)

PROGRAM SCOPE

This project investigates fundamental problems associated with visible light-driven water splitting in molecular photoelectrochemical systems. In natural photosynthesis, light-absorbing molecules are coupled to chains of electron donors and acceptors that drive electrochemical oxidation and reduction reactions using enzymatic catalysts. The example of natural photosynthesis suggests that it should be possible to design efficient functional mimics by combining photoredox molecules, electron relays, and nanoparticle catalysts. This goal has been elusive so far because of the problem of controlling back

electron transfer reactions, which are often much faster than the catalytic reactions that make hydrogen and oxygen. In this project, the oxidative half-cycle of water splitting is carried out using dye molecules coupled to water oxidation catalysts on porous semiconductor electrodes. The reduction of water is driven by light at a photocathode consisting of dye molecules, semiconducting oxide sheets, electron relays, and nanoparticle catalysts. Both arrangements provide control over the distances between components at the nanometer length scale. Transient spectroscopy and electrochemical methods are used to measure the rates of forward and back electron transfer. Molecular design and spectroscopic methods are used to control and understand electron transfer at the molecule-nanoparticle catalyst interface. The problem of proton management in water splitting photosystems is also being studied by electrochemical methods.

FY 2014 HIGHLIGHTS

This project had earlier demonstrated overall water splitting in a molecule-based system, using ruthenium tris(bipyridyl) dyes coupled to iridium oxide nanoparticles on high surface area TiO₂ electrodes. Several groups have since made similar photoanodes using different molecular catalysts and have achieved photocurrents in the mA range, comparable to some of the best oxide photoelectrode materials for water splitting. A problem with the molecular system, not understood before this year, is the rapid polarization of the photoanode. We have now developed a full kinetic model of the photoanode that explains the polarization, and have used dynamic measurements (photovoltage decay, electrochemical impedance spectroscopy) to measure the relevant kinetic parameters. These measurements suggest that more efficient systems will be possible using core-shell electrode structures and molecular catalysts. They also elucidate the important role of surface protonation in back electron transfer. For photoelectrolysis cells that operate near neutral pH, proton management across the membrane that separates the anode and cathode is a significant problem. Our earlier work showed that pH gradients develop in such cells because the transference number of protons is less than unity. We have recently investigated bipolar membranes for use in these cells and showed that they enable water splitting with low losses when the anode and cathode operate at high and low pH, respectively. This finding is promising for developing water and CO₂ electrolysis systems that operate at low overpotentials using earth-abundant photoelectrode and catalyst materials.

First-Row Transition Metal-Based Chromophores for Dye-Sensitized Solar Cells: Fundamental Issues and Applications

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Funding: \$181,000 (2014)

PROGRAM SCOPE

The overall focus of this research program is to explore the fundamental science underpinning the notion of using first-row transition metal complexes as chromophores in solar energy conversion strategies. These compounds hold the promise of having a transformative impact on solar energy science due to their earth-abundant nature, but do not perform well relative to their 2nd- and 3rd-row counterparts in strategies that require photo-induced charge separation. Our hypothesis for why this is

the case is that the nature of the electronic structure of 1st-row metal complexes (e.g., compounds of Fe(II)) results in ultrafast deactivation to lower-lying electronic states such that they are not kinetically competitive with processes such as interfacial electron transfer (as required in a dye-sensitized solar cell) or bimolecular electron transfer (as might occur when coupling light absorption to a catalyst). This hypothesis is supported by a string of significant observations stemming from research directly funded by DOE's Solar Photochemistry program and is now a generally accepted paradigm in the photo physics and solar energy community. The specific goal of the research program is to (1) identify the key factors that are responsible for driving these ultrafast excited-state processes, i.e., the conversion of charge-transfer excited states to lower-energy ligand-field excited states, and (2) to use this knowledge to inform synthetic design for the realization of chromophores that can be incorporated into solar energy conversion schemes that currently require rare, more expensive components such as ruthenium.

FY 2014 HIGHLIGHTS

Research during FY2014 has been focused on two specific themes within the broader goals outlined in the previous section. First, we have developed chemistry allowing for the synthetic elaboration of the dcpp ligand. The Fe(II)-bis adduct of this compound, published in 2014, was a breakthrough discovery for us insofar as it offered the possibility of altering the electronic structure of an Fe(II) complex such that it would resemble its 2nd- and 3rd-row congeners in terms of the relative energetic ordering of its charge-transfer and ligand-field excited states. Specifically, we believe that we have identified the key aspect of this compound's composition that is responsible for its unique optoelectronic properties; this discovery is going to fuel a significant portion of our research in this area and will be described in a renewal proposal that will be submitted next month. We have also developed the necessary chemistry to functionalize this ligand system for attachment to semiconductor nano particles for testing in dye-sensitized solar cells. The second theme has involved a more detailed examination of structural features that appear to be driving ultrafast surface crossings in this class of compounds. Ultrafast time-resolved absorption measurements have revealed a clear sensitivity to geometric distortions about the primary coordination sphere of the metal center. We have therefore designed new ligand frameworks around this idea in an effort to modulate the dynamics sufficient for electron transfer processes out of the charge-transfer states to become kinetically competitive. This is going to be coupled to a new effort in the group - variable-temperature ultrafast time-resolved absorption spectroscopy - that will be pursued in the next phase of the research program so that we can obtain more quantitative information about the nature of the barriers associated with the ultrafast dynamics that undermine the utility of this class of chromophores.

Metal-to-Ligand Charge Transfer Excited States at Interfaces and in Rigid Media

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Funding: \$181,000 (2014)

PROGRAM SCOPE

Photo-Induced, Interfacial Electron Transfer at the Transparent Oxide-Solution Interface and Long Range Electron and Energy Transfer in Polymer Films are being investigated for possible applications in energy conversion processes.

FY 2014 HIGHLIGHTS

Photo-induced interfacial electron transfer to and from nanoparticle, mesoscopic thin films of conducting transparent conducting oxides (TCO) is under investigation for possible applications in energy conversion. Excitation, injection and back electron transfer by Ru(II) polypyridyl complexes, surface-bound to Sn-doped In_2O_3 (nanoITO) in acetonitrile solutions have been investigated by transient absorption measurements. Excitation of the metal-to-ligand charge transfer (MLCT) excited states of these complexes is followed by efficient excited state electron injection with injection efficiencies of $\sim 100\%$. Injection occurs on the picosecond time scale and back electron transfer (BET) on the nanosecond time scale. By varying the external bias, the influence of driving force on electron transfer was investigated over a range of 1.8 eV. Kinetics data for electron injection and BET were analyzed by application of Marcus-Gerischer theory to obtain key fundamental electron transfer parameters - reorganization energy and electronic coupling matrix element - for both injection and BET. These results demonstrated the versatility of nanoTCOs as a tool for studying photo-induced electron transfer reactions relevant to solar energy conversion in dye-sensitized devices. The photophysical and photochemical properties of a series of Ru(II) and Os(II) polypyridyl MLCT excited-states were investigated at the fluid-to-film transition in a poly(ethyleneglycol) (PEG). In PEG films with added anthracene derivatives, long-range energy transfer and energy transfer followed by electron transfer have been observed by transient absorption measurements. MLCT emission energies in the PEG fluid increase following thermal polymerization to give semi-rigid films which enhances emission and lifetimes consistent with the energy gap law for non-radiative excited-state decay.

Singlet Fission

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

It was proposed to combine experimental and theoretical tools to improve the presently unsatisfactory understanding of the singlet fission process to a level that will allow efficient design of (i) new singlet fission chromophores with optimal excitation energies, about 2.2 eV for S_1 , and about 1.1 eV for T_1 ; (ii) optimal modes of inter-chromophore coupling. The goal is the development of a predictive competence for the design of useful materials for 200% triplet yield from singlet fission in a dimer, oligomer, aggregate, polymer, or solid. Our laboratory is set up to perform organic synthesis, spectroscopic and photophysical measurements, and quantum chemical calculations, and we have prior experience in all of these.

FY 2014 HIGHLIGHTS

We are seeking access to efficient singlet fission (SF) materials using theory, synthesis, and photophysics, collaborating with a group at NREL and with a Czech theoretician. We have used the diabatic approximation and a model that considers the HOMO and the LUMO of each chromophore in a dimer. For approximately isoergic SF, we have a formula for the Fermi Golden Rule matrix element TRP, with a term for a direct interaction of the initial and final states and a term for interaction mediated by virtual charge transfer states. The formula for TRP was evaluated (i) exactly, (ii) with neglect of intermolecular overlap, and (iii) with neglect of zero differential overlap. The mediated term dominates. Case (iii) only requires knowledge of Hückel MOs and overlaps between AOs on the chromophores. We proposed that biradicaloids are a likely source of new SF chromophores and identified several promising ones. We examined SF in 1,3-diphenylisobenzofuran (1), many of its covalent dimers, and a polymer. One of the two crystalline modifications is about 20 times more efficient than the other, although their crystal structures are very similar. A carboxylic acid derivative was adsorbed on TiO₂ nanoparticles coated with a thin layer of ZrO₂ and an optimal ZrO₂ thickness allowed injection from T₁ produced by SF to dominate over injection from S₁. In polar solvents, excitation of weakly coupled dimers produced a directly observable CT intermediate (two-step SF). Among directly coupled dimers, the p,p isomer is interesting since we observe a planar and a twisted conformers of both S₀ and T₁, with excitation delocalized in the former and localized on one half of the dimer in the latter. A polystyrene carrying 1 on each repeat unit showed no SF in solution. We have examined two polymorphs of the biradicaloid dye cibalackrot. In each, the Davydov splitting is 0.2 eV, making SF endoergic.

Electrochemical and Spectroscopic Investigations of H₂O Oxidation by Porous Coordination Network Catalysts

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Funding: \$450,000 (2014-2017)

PROGRAM SCOPE

Metal organic frameworks (MOFs), 3D crystalline porous coordination networks of metal ions connected in close proximity by multi-dentate organic linkers, have tremendous potential for use in catalysis. Molecular secondary building units assemble to produce largely porous materials with the highest surface areas reported. This surface area can be exploited to produce higher catalytic reaction rates than those observed with traditional heterogeneous or homogeneous approaches. Capitalizing on this advantage, the proposed research aims to explore MOF materials for photoelectrochemical water oxidation. Specifically, the project will (1) identify MOF materials capable of electrochemical water oxidation, and (2) integrate these MOFs as thin films on semiconductor surfaces for photoelectrochemical activation. The proposal focus will be on in-depth electrochemical and spectroscopic studies of reactivity and mechanism to elucidate the design constraints of such catalysts. MOF catalyst candidates have been identified based on the following criteria: (1) the MOF must be stable in aqueous solution, preferably over a wide range of pH; (2) include a redox active metal sites; and (3) exhibit high internal surface area. Exploration of MOF water oxidation catalysts and photoelectrochemical MOF behavior is in its infancy and our studies represent the first to combine the

two concepts. Therefore, accomplishing the aforementioned goals will provide new discoveries about the structure–function relationship of MOFs and allow the rational design of next generation MOF-H₂O oxidation catalysts. Once developed, a complete H₂O oxidation system will improve the nation’s energy profile by providing a means to store solar energy. Thus, this proposal describes a series of unique materials and fundamental studies that hold the potential for unparalleled environmental and economic impacts.

FY 2014 HIGHLIGHTS

Funding for this project began June 1, 2014. In the initial 3 months, we have collected preliminary data on two MOF constructs that are viable for water oxidation catalysis. The first construct utilizes the nodal clusters of cobalt and palladium-based MOFs to facilitate water oxidation. These redox active centers are connected by an organic linker capable of intraMOF proton transfer to facilitate proton-coupled electron transport. A complete electrochemical analysis has been conducted on the two materials and catalysis occurs at moderate overpotential with impressive catalytic rates. We expect to publish these results within the next funding period. The second construct incorporates known small molecular water oxidation catalysts (ruthenium and copper-based) into water-stable MOF backbones with zirconium and lead-based nodal clusters. The small molecule catalysts have been studied in homogeneous solution in this initial funding period and both efficiently oxidize water electrochemically. We will expand this work to MOFs within the next funding period.

Hangman Catalysts for Photo- and Photoelectrochemical Activation of Small Molecules

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Funding:	\$228,000 (2014)

PROGRAM SCOPE

Solar-to-fuels generation requires the rearrangement of stable chemical bonds with light as the impetus for the fuel-forming reaction. All such reactions, regardless of the specific fuel, require the transfer of multiple electrons and protons. Energy barriers to such bond rearrangements are minimized only if electrons are efficiently coupled to protons. A catalyst can mediate this coupling, and as well as it does so, will determine the solar-to-fuels efficiency. The scope of this project includes several aspects of this energy conversion process as it applies to hydrogen and oxygen production from water, carbon dioxide reduction for the purposes of yielding a liquid fuel (in place of hydrogen) and the complementary fuel cell reaction, oxygen reduction by hydrogen (fuel cell reaction). In this program, a new class of catalysts—called Hangman catalysts—is under study with an eye towards water splitting. In Hangman constructs, an acid-base functionality is poised over a redox active metal platform. On a mechanistic front, the Hangman systems orthogonalize Proton Coupled Electron Transfer (PCET) and in doing so they permit control of proton transfer over short distances and electron transfer over long distances. Hangman catalysts comprising porphyrin, corrole and chlorin macrocycles have been explored for promoting reactions of oxygen reduction (fuel cell catalysts), O₂ and H₂ production from water (solar energy catalysts) and CO₂ reduction (liquid fuels). The physical and chemical properties of the Hangman catalysts are varied in order to define the optimal conditions in which the aforementioned energy

conversion reactions may be best carried out. Using picoseconds and nanosecond laser methods, we have begun setting the groundwork to observe bond forming steps in real time.

FY 2014 HIGHLIGHTS

Work during the past funding cycle has focused on: (1) adapting and elaborating synthetic methods to enable the delivery of hangman macrocycles in sufficiently high yields and quantities to enable PCET studies to be undertaken with facility; (2) designing hangman macrocyclic platforms that promote the HER reaction with an emphasis on elucidating key intermediates via the construction of mechanistic models. During 2014, we have shown that Co hangman porphyrins catalyze HER from weak (benzoic) and strong (tosic) acids in acetonitrile solutions. Electrokinetic mechanistic studies of HER were consistent with formation of the Co(II) hydride by stepwise electron-transfer followed by proton transfer (ET-PT). Catalytic enhancement by the hangman moiety arose from a rapid intramolecular rate-limiting PT (ca. $8.5 \times 10^6 \text{ s}^{-1}$). This is the first direct measure of a proton transfer rate in a HER conversion and our results indicate that the presence of the pendant proton relay proximate to the metal center gives rise to a rate enhancement that is equivalent to an effective benzoic acid concentration $>3000 \text{ M}$. This is the first quantitative measurement of the benefits of a pendant proton transfer in the secondary coordination sphere of a HER catalyst. Studies were expanded to iron hangman porphyrins with a larger cleft to allow for the accommodation of a diverse set of hanging groups possessing different steric and acid/base properties. The key step in obtaining this library relied on the synthesis of a precursor that contained an aldehyde functionality and a protected carboxylic acid (methyl ester). The chemistry was carried out in four steps on a decagram scale in 37% overall isolated yield. We employed the foot-of-the-wave analysis (FOWA) to analyze the electrocatalytic reduction of protons to hydrogen and CO_2 to CO and H_2O .

Studies of Photoinduced Electron Transfer from Dyes, Polymers and Quantum Confined Systems into Semiconducting Single Crystals

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

The project has studied the sensitization of many single crystal oxide semiconductors as well as gallium phosphide with both sensitizing dyes and quantum dots. Some light absorbing polymers were also studied.

FY 2014 HIGHLIGHTS

Mott-Schottky analysis is used to determine the band-edge positions for ZnO single crystals in acetonitrile electrolytes. The band alignment between ZnO and PbS QDs suggests that electron injection can occur for PbS quantum dots (QDs) over a wide range of sizes. Sensitization of ZnO single crystal electrodes with PbS QDs is then demonstrated using ferrocene/ferrocenium as the regenerator (hole acceptor). The largest 5.5 nm QDs are sensitizing the ZnO out to 1580 nm or 0.84 eV, to our knowledge

the longest wavelength sensitization measured for any oxide semiconductor. The driving force for the hole transfer from the 5.5 nm PbS QDs with a band gap of 0.84 eV using ferrocene/ferrocenium regenerator in acetonitrile was found to be close to zero which may result in a high open circuit voltages for QDs sensitized solar cells (QDSSCs) with a spectral response extending well into the infrared. Homoepitaxial growth of highly ordered and pure layers of rutile on rutile crystal substrates and anatase on anatase crystal substrates using atomic layer deposition (ALD) was accomplished. The epilayers grow in a layer-by-layer fashion at low deposition temperatures but are still not well ordered on rutile. Subsequent annealing at higher temperatures produces highly ordered, terraced rutile surfaces that in many cases have fewer electrically active defects than the substrate crystal. The anatase epitaxial layers, grown at 250°C, have much fewer electrically active defects than the rather impure bulk crystals. Annealing the epilayers at higher temperatures increased band gap photocurrents in both anatase and rutile.

Transition Metal Polypyridine Complexes: Studies of Mediation in Dye-Sensitized Solar Cells and Charge Separation

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Students: 1 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding: \$360,000 (2014-2015)

PROGRAM SCOPE

The research comprises two problems in solar photoconversion. The first considers photoinduced charge separation within the context of discrete molecular assemblies composed of a chromophore simultaneously linked to an electron donor(s) and an electron acceptor(s).

The second considers photoinduced charge separation in dye-sensitized solar cells. In each of these platforms, absorbed light initiates a cascade of electron transfer events, the relative rates of which determine the final outcome. The interplay between many factors (thermodynamic driving force, reorganization energy, donor-acceptor electronic coupling, mass transport and spin dynamics) control those rates and thus define the processes efficiency. Through appropriate structural and energetic manipulation of the molecular charge-separation and –transport machinery it is possible to gain fundamental mechanistic insight about the relevant electron transfer processes involved.

FY 2014 HIGHLIGHTS

No FY14 Highlights provided

Catalysis and Light Harvesting at Interfaces-Focus on Solar Fuels

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Funding: \$360,000 (2014-2015)

PROGRAM SCOPE

In artificial photosynthesis, an effective way to store solar energy is to convert it into chemical energy via the rearrangement of chemical bonds. The water oxidation reaction plays a crucial role in this process. The main challenge towards the future use of artificial photosynthesis is the development of economically feasible catalysts for water splitting. This catalyst will work as a part of an integrated assembly for light driven water splitting. The goal of this proposal is to determine the structure and electronic configurations of the critical intermediates of water oxidation as well as their dynamics under catalytic conditions. Time resolved techniques will be used to monitor the evolution of electronic states during the water oxidation and light harvesting. The relationship between molecular structure and catalytic activity will be uncovered and reaction barriers will be modeled based on experimental information. The informative techniques to study *in situ* catalytic water oxidation and dynamic of light harvesting are synchrotron-based X-ray spectroscopy, including X-ray absorption near edge structure (XANES), extended X-ray absorption fine structure (EXAFS) and X-ray emission spectroscopy (XES), electron paramagnetic resonance (EPR) and multiwavelength kinetic resonance Raman spectroscopy. These experimental techniques will deliver information on the structure of the intermediates and their electronic configuration and evolution of samples during the catalytic processes *in situ*. Ultimately, the results of the proposed research will constitute a major step towards development of future light-to-fuel energy solutions, thus contributing to the US security through energy independence and will help to reduce greenhouse gas emissions.

FY 2014 HIGHLIGHTS

As a research highlight we would like to list our publication "Spectroscopic analysis of catalytic water oxidation by $\text{Ru}^{\text{II}}(\text{bpy})(\text{tpy})\text{H}_2\text{O}]^{2+}$ suggests that $\text{Ru}^{\text{V}}=\text{O}$ is not a rate-limiting intermediate" by Yulia Pushkar, Dooshaye Moonshiram, Vatsal Purohit, Lifan Yan, Igor Alperovich, Journal of the American Chemical Society, 2014, 136 (34), pp 11938–11945. Modern chemistry's grand challenge is to significantly improve catalysts for water splitting. Further progress requires detailed spectroscopic and computational characterization of catalytic mechanisms. We analyzed one of the most studied homogeneous single-site Ru catalysts, $[\text{Ru}^{\text{II}}(\text{bpy})(\text{tpy})\text{H}_2\text{O}]^{2+}$ (where bpy = 2,2'-bipyridine, tpy=2,2';6',2''-terpyridine). Our results reveal that the $[\text{Ru}^{\text{V}}(\text{bpy})(\text{tpy})=\text{O}]^{3+}$ intermediate, reportedly detected in catalytic mixtures as a rate limiting intermediate in water activation is not present as such. Using a combination of EPR and X-ray absorption spectroscopy, we demonstrate that 95% of the Ru complex in the catalytic steady state is of the form $[\text{Ru}^{\text{IV}}(\text{bpy})(\text{tpy})=\text{O}]^{2+}$. $[\text{Ru}^{\text{V}}(\text{bpy})(\text{tpy})=\text{O}]^{3+}$ was not observed and according to DFT analysis might be thermodynamically inaccessible at our experimental conditions. A reaction product with unique EPR spectrum was detected in reaction mixtures at about 5% and assigned to Ru^{III} -peroxo species with (-OOH or -OO- ligands). $[\text{Ru}^{\text{II}}(\text{bpy})(\text{tpy})\text{H}_2\text{O}]^{2+}$ is the simplest representative of a larger class of water oxidation catalysts with neutral, nitrogen containing heterocycles. We expect this class of catalyst to work mechanistically in a similar fashion via $[\text{Ru}^{\text{IV}}(\text{bpy})(\text{tpy})=\text{O}]^{2+}$ intermediate unless more electronegative (oxygen containing) ligands are introduced in the Ru coordination sphere, allowing the formation of more oxidized Ru^{V} intermediate.

Energy, Electron Transfer and Photocatalytic Reactions of Visible Light Absorbing Transition Metal Complexes

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Funding: \$80,000 (2014)

PROGRAM SCOPE

Effective systems for photochemical reduction of water to hydrogen must involve efficient approaches for using sunlight to generate chemical reductants to provide electrons necessary for catalysts to combine with protons from water to yield hydrogen. A parallel avenue of research is development of the catalysts. In the end systems containing a light-absorbing unit, an electron relay and a catalyst must be combined and evaluated under laboratory and solar irradiation conditions. Our group has worked on making highly reliable photochemical systems in an effort to clearly evaluate the efficiency of various catalysts under solar photochemical conditions. This is a necessary step for comparison of catalytic systems being developed (there are many). Our work here includes testing water reduction catalysts made in other labs and we have a variety of collaborations with chemists developing new, more effective catalysts. Another objective that is a continuation of earlier work is the investigation of the photochemistry and light induced electron transfer reactions of square planar Pt(II) imine complexes, principally terpyridyl complexes. Through a thorough examination of light induced one electron reduction and oxidation reactions of the Pt(II) complexes and the subsequent thermal reactions of the unstable intermediate species (Pt(III) or Pt(I)), the factors influencing net two-electron reaction of the complexes can be understood. Of particular interest are processes that result in one electron oxidation of the Pt(II) complex, because the Pt(III) intermediates generated are highly reactive and could yield photoproducts that ultimately react further to regenerate the Pt(II) complex and also yield an oxidized substrate; for example, it may be possible to oxidize water to hydrogen peroxide via a photocatalytic cycle.

FY 2014 HIGHLIGHTS

Highlights for the group in FY 2014 include development of new photochemical systems for generation of very strong reducing agents in aqueous and nonaqueous solutions. The systems are air stable until photolyzed and are capable of serving as reductants for a wide range of water reduction catalysts aimed at generation of hydrogen (see *J. Phys. Chem.* v. 118, p.10400). A key to making the systems was employing coupled near self-exchange electron transfer reactions between reversible electron donors and sacrificial electron donors. A second highlight involves development of new visible light absorbing sensitizers for photoinduced electron transfer reactions that consist of earth abundant metal complexes (Sn(IV)) that can serve as substitutes for the more commonly used noble metal complexes (see: *Dalton Transactions*, v. 43, p. 17754). These chromophores form triplet excited states in high yield, but have been heretofore ignored because they do not exhibit phosphorescence. A third highlight illustrates the use of ultrafast time resolved infrared spectroscopy to follow the flow of electron density upon creation of an excited state (in Re(I) carbonyl complexes) and subsequent intramolecular electron transfer events that result in what can best be described as partial charge transfer (see: *J. Phys. Chem. B*, v. 117, p. 15903). The system involves a delocalized hole between the metal center and a dimethylamino moiety on one of the coordinated ligands. The work, in collaboration with Igor Rubtsov (Tulane), has been expanded to other systems wherein full charge separation occurs; changes in infrared stretching frequencies of the carbonyl ligands provide clear and dramatic evidence for the shifts in electron density following visible light excitation.

Organic, Nanoscale, and Self-Assembled Structures Relevant to Solar Energy Conversion

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Funding: \$171,000 (2014)

PROGRAM SCOPE

This program seeks to understand the molecular-level principles by which complex chemical systems carry out photochemical charge separation, transport, and storage, and utilize these principals to impact the design of practical solar energy conversion and storage devices. Towards this goal, this program focuses on: (i) delineating new compositions of matter relevant to solar energy conversion, (ii) understanding the basic photophysical properties of next-generation conjugated materials for excitonic solar cells, (iii) elucidating rules and principles relevant to controlling charge transfer, charge migration, photoconductivity, and exciton diffusion dynamics in structures and assemblies pertinent to light-driven energy transduction, (iv) probing the extent of electronic coupling between conjugated organic materials and nanoscale structures in both ground and excited states, and (v) engineering high quantum yield electron-hole pair production from initially prepared excitonic states in organic materials and organic compositions that feature nanoscale, electrooptically active components.

FY 2014 HIGHLIGHTS

Single-Handed Helical Wrapping of Single-Walled Carbon Nanotubes by Chiral, Ionic, Semiconducting Polymers. We have established the requisite design for aryleneethynylene polymers that give rise to single-handed helical wrapping of single-walled carbon nanotubes (SWNTs). Aryleneethynylene polymers were synthesized that feature a 2,2'-(1,3-benzyloxy)-bridged (b)-1,1'-bi-2-naphthol unit: this 1,1'-bi-2-naphthol derivative is characterized by a bridging 2,2'-1,3 benzyloxy tether that restricts the torsional angle between the two naphthalene subunits along its C1-C1' chirality axis to larger, oblique angles that facilitate more extensive van der Waals contact of the naphthyl units with the nanotube. Related semiconducting polymer-SWNT superstructures have been realized that demonstrate that the combination of single-handed helical wrapping and electronic structural modification of conjugated polymer motif opens up new opportunities for engineering the electro-optic functionality of nanoscale objects. Ionic Self-Assembly Provides Dense Arrays of Individualized, Aligned Single-Walled Carbon Nanotubes. Developing the means to control single-walled carbon nanotube (SWNT) organization in multi-component ensembles has been a long-standing goal. We demonstrated for the first time that SWNTs, helically wrapped by a single chain of an anionic [arylene]ethynylene polymer, can be structured into organized microscale objects through ionic self-assembly (ISA). These microstructures are composed of rigorously aligned nanotubes at high areal density (2.5×10^{10} SWNTs cm^{-2}), and maintain the optical properties characteristic of individualized SWNTs. We posit that the combination of chiral polyanionic polymers, SWNTs having electronic structural homogeneity, the ability to modulate polymer electronic structure by design, and the facility of ISA to provide hierarchical organization, offers exceptional promise for the development of new types of electro-optic materials.

Further Studies on Photocatalytic Water Decomposition

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Funding: \$382,000 (2014-2015)

PROGRAM SCOPE

This project involves the design, synthesis, and study of chromophore-catalyst assemblies that will use energy inherent in the photoexcited state of the chromophore to activate a catalyst that in turn will carry out the bond breaking and bond making steps required for the conversion of water into its elements. Such assemblies can be envisioned to accomplish both the reduction of protons to make hydrogen and the oxidation of hydroxide to make oxygen. As long as these two processes are separate, however, a sacrificial electron donor or acceptor will be necessary to complete the catalytic cycle. An important objective is to integrate these processes and thereby avoid sacrificial reagents. We have discovered a family of mono- and dinuclear Ru(II) complexes that are efficient catalysts for water oxidation. These catalysts possess polypyridine ligands and are classified as Type I, II, and III catalysts. Current studies concentrate on the Type III catalyst having a tetradentate dipyriddyphenanthroline (dpp) equatorial ligand. The isolation of a dpp di-N-oxide Ru complex during the generation of O₂ has evoked the interesting question as to whether this species might be an intermediate in the oxidation process. Parallel studies are aimed at the development of water reduction catalysts based on Co(II) and Ni(II). A Co(II) polypyridine catalyst has been discovered that affords light-driven H₂ production (TON > 300 h⁻¹) in pure water. By ligand modification we will optimize and modify this system to improve performance and to allow incorporation into a dyad assembly. Bridging ligands will be explored with respect to the ability to gate and direct electron flow.

FY 2014 HIGHLIGHTS

We have prepared the ligand 8-(1',10'-phenanthroline-2'-yl)-2-(pyridin-2'-yl)quinoline (ppq) that contains an additional sp² carbon (C₈ of quinoline). This ligand readily accommodates Co(II) to form [Co(ppq)Cl₂]. The critical precursor to ppq can be accessed by either the Friedländer condensation of 3-bromo-2-aminobenzaldehyde with 2-acetylpyridine or the selective Stille coupling of 2-pyridyl-tri-n-butylstannane with 2,8-dibromoquinoline. In a similar fashion a variety of ppq derivatives have been prepared. To measure evolved hydrogen by these complexes, we developed a reactor in which the internal pressure is monitored by a transducer in real time. Properly used, this method is useful for measuring either hydrogen or oxygen. We have prepared a series of dyad assemblies C-L-P where C = water oxidation catalyst derived from [Ru(tpy)(bpy)(I)]⁺, P = a photosensitizer derived from [Ru(bpy)₂(phen)]²⁺, and L is a linker that consists of a combination of ethynylene or phenylene moieties. These systems are being evaluated for light-driven water oxidation. Together with our collaborators at Brookhaven National Lab, we have been examining a series Ru(II) water oxidation catalysts that involve a meridional quaterpyridine-type ligand. During water oxidation by the complex [Ru(dpp)(pic)₂]²⁺ (dpp = 2,9-di-(pyridin-2'-yl)-1,10-phenanthroline, pic = 4-picoline) we isolate a Ru(II)-complexed di-N-oxide intermediate and are in the process of determining the origin of this species and its importance in the water oxidation process. A 6-5 chelator is a tridentate ligand that binds a metal forming both a five and six-membered chelate ring. It appears that this less strained situation allows for water attack on the oxidized metal

center to form a seven-coordinate pentagonal bipyramid intermediate that is not accessible from a 5-5 chelator. Unlike $[\text{Ru}(\text{tpy})_2]^{2+}$, these complexes are active as water oxidation catalysts.

Photocatalysts for H_2 Evolution: Combination of the Light Absorbing Unit and Catalytic Center in a Single Molecule

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Funding: \$158,000 (2014)

PROGRAM SCOPE

The search for renewable, clean sources of energy is critical for the future of the planet. The use of abundant sunlight to generate electricity or to efficiently and catalytically transform inexpensive simple molecules into clean fuels, such as the splitting of water into H_2 and O_2 , remains a challenge. This research project aims to design and develop single-component photocatalysts for the reduction of protons to hydrogen, whereby the light absorbing (LA) unit and hydrogen-evolving center (HEC) are combined within a single molecule. Combining function-specific molecular components decreases the number of required bimolecular charge transfer processes, often a cause of limited efficiency in photocatalytic systems. The use of a redox-active $\text{Rh}_2(\text{II},\text{II})$ dimeric core whose light absorbing, electrochemical, and excited state properties are modulated by electron-donating formamidinate and electron-accepting polypyridyl ligands provides insight into the interplay between each component and how this impacts overall catalysis. This strategy employs bimetallic complexes with highly reducing excited states and open coordination sites to function as both the LA and HEC.

FY 2014 HIGHLIGHTS

Collaborative efforts between the Turro (The Ohio State Univ.) and Dunbar (Texas A&M University) research labs have led to the synthesis of multiple formamidinate-bridged $\text{Rh}_2(\text{II},\text{II})$ dimers. Varying the electron-accepting ability of the neutral, bidentate polypyridyl ligand tunes the LUMO within the molecule, impacting the reductive capabilities and pathways within catalysis. Conversely, modifying the electron-donating ability of the anodic formamidinate bridging ligands modulates the electron density at the $\text{Rh}_2(\text{II},\text{II})$ core and therefore the HOMO. Electrochemical studies and DFT calculations confirm the impact that formamidinate and polypyridyl ligands have on the energies of the molecule's HOMO and LUMO, respectively. In depth electrocatalytic studies revealed some of the thermodynamic and kinetic aspects of catalytic proton reduction to hydrogen using this $\text{Rh}_2(\text{II},\text{II})$ architecture. Addition of a weak acid (CH_3COOH , $\text{pK}_a = 13.5$ in DMF) in organic solutions displays the rapid turnover frequency, TOF, of 10^4 s^{-1} , of this system functioning at a mild overpotential ($\text{OP} = 0.45 \text{ V}$). These studies also provide insight into the mechanism of hydrogen evolution, with the current description suggesting formation of a $\text{Rh}_2(\text{II},\text{I})$ core, followed by protonation to give a $\text{Rh}_2(\text{II},\text{III})$ -hydride species before further protonation and reduction to evolve hydrogen and regenerate the catalyst. Currently, a manuscript for submission in a peer-reviewed journal detailing the electrocatalysis findings is underway. Future work within the FY 2015 includes continued synthesis of strong visible light absorbing $\text{Rh}_2(\text{II},\text{II})$ dimers, increasing the excited state lifetime within these dimers, and inclusion of anchoring substituents for coordination to semiconductor electrodes and nanoparticles.

A Concerted Synthetic, Spectroscopic, and Computational Approach Towards Water Splitting by Heterometallic Complexes in Solution and on Surface

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Funding: \$418,000 (2014)

PROGRAM SCOPE

The basic premise of this collaborative project is the investigation of monometallic modules and multimetallic modular complexes in solution and on surfaces. We aim to understand the requirements necessary to effective electron transfer in antenna/catalyst/acceptor modules of a single molecule, as well as the mechanisms of photo and electrocatalytic proton and water reduction and water oxidation. The modular antenna is aimed to function as a sensitizer absorbing solar radiation and generating an excited state able to transfer an electron. For proton and water reduction this electron is supposed to be transferred directly to the catalyst module, whereas water oxidation requires that ET involves an acceptor module in order to provide a hole to the catalyst module, thus implying that the metal center will be able to reach a highvalent oxidation state. Aiming to use Earth-abundant metals, we have focused our efforts on cobalt-containing modules for reduction and manganese-containing modules for oxidation. Study of new modular catalysts starts with the evaluation of their electrocatalytic properties, and we aim to attach the most promising catalysts to ruthenium-based antenna modules. Therefore, emphasis has been given to monometallic modules containing cobalt and ruthenium ions. The Verani group is responsible for syntheses, electrochemical, and catalytic studies, while the Endicott group focuses on the photochemistry and photophysical aspects and the Schlegel group provides DFT and TD-DFT calculations. For the long run, the relevance of this work relates to a new class of integrated [acceptor/antenna/active site] photocatalysts that allow for generation of dihydrogen and dioxygen from water.

FY 2014 HIGHLIGHTS

In a close and interactive collaboration, the Verani and Schlegel groups have studied the behavior of two series of electrocatalysts capable of proton and water reduction. We investigated the redox, spectroscopy, and catalytic reactivity of new cobalt(III) complexes $[\text{Co}^{\text{III}}(\text{LPhOX})\text{MeOH}]$, based on phenolate-rich $[\text{N}_2\text{O}_3]$ ligands, where X indicates the presence of chloro, bromo, iodo, or tert-butyl substituents in the 3rd and 5th positions of each phenolate ring. The Cl^- species reduces effectively protons in weakly acidic media with a TON of 11 after 3 h of bulk electrolysis at $-2.20 \text{ V}_{\text{Fc}/\text{Fc}^+}$. We also studied a series of cobalt complexes $[\text{Co}^{\text{III}}(\text{LP}_y)\text{Cl}]$ with pentadentate pyridine-rich ligands. An initial Co(II) amine complex is prone to aerial oxidation yielding a Co(III) imine complex that is further converted into an amide complex in presence of adventitious water. Introduction of an N-methyl protecting group to the ligand inhibits this oxidation and gives rise to a Co(II) species. Both the amide and Co(III) and methylated Co(II) show electrocatalytic H_2 generation in weakly acidic media with TONs of ca. 15 after 3h at -1.9 V vs. Fc^+/Fc . Remarkably these complexes are soluble in water and yielded TON of 7,000 after 18 h. Mechanisms of catalysis seem to involve the protonation of a $\text{Co}^{\text{II}}\text{-H}$ species generated *in situ*, and no indication of proton-coupled electron transfer was observed. The Endicott and Schlegel groups have

found that most of the observed variations in $^3\text{MLCT}$ excited state distortions, emission intensities and to some degree lifetimes of Ru-(aromatic ligand) complexes arise from configurational mixing with higher energy ligand centered excited states. A major factor determining $^3\text{MLCT}$ excited state lifetimes, especially under ambient conditions, is the relative energies of the lowest energy $^3\text{MLCT}$ and triplet metal centered excited states (^3MC).

Approaches to Integrated Photochemical Systems for Solar Energy Conversion

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Funding: \$304,000 (2014)

PROGRAM SCOPE

Natural photosynthesis is carried out by organized assemblies of photo-functional chromophores and catalysts within proteins, which provide specifically tailored environments to optimize solar energy conversion. Artificial photosynthetic systems for practical solar fuels and electricity production must collect light energy, separate charge, and transport charge to catalytic sites where multi-electron redox processes for fuel formation will occur or to electrodes where charge is collected for electricity production. The primary goal of our research is to understand the fundamental principles needed to develop integrated artificial photosynthetic systems. These principles include how to promote and control within complex molecular systems: 1) energy capture, charge separation, and long-range directional energy and charge transport, 2) coupling of separated charges to multi-electron catalysts for fuel formation, and 3) supramolecular self-assembly for scalable, low-cost processing from the nanoscale to the macroscale. Identifying and determining the dynamics of both short- and long-lived intermediates produced by photo-initiated charge separation and transport in complex molecular systems is critical to understanding how to design functional artificial photosynthetic systems. We employ synchrotron-based X-ray diffraction and scattering techniques to characterize molecular structures and assemblies. We also use femtosecond transient absorption, fluorescence, stimulated Raman, and IR spectroscopy to study ultrafast energy and charge transfer dynamics in these systems, while we use time-resolved pulsed-EPR spectroscopy to probe the nanosecond and longer timescale dynamics of the paramagnetic intermediates. These techniques provide the detailed structural data essential to understanding how to design integrated molecular systems for photochemical solar energy conversion.

FY 2014 HIGHLIGHTS

We have shown that singlet exciton fission (SF) occurs in high yield (170%) in robust perylene diimide (PDI) polycrystalline solid films aided by crystal engineering of a slip-stacked structure. We have also shown that crystal engineered terrylenes (the longer homolog of perylene) have SF performance approaching the theoretical maximum of 200%. Moreover, comparing our PDI and terrylene data shows that if SF is exoergic, then the structural requirements for high efficiency SF are somewhat relaxed, while if SF is endoergic these structural requirements are much more restrictive. This discovery is important for designing solar cells based on SF. We have developed columnar, ordered zinc tetrabenzoporphyrin-PDI assemblies that undergo single-step charge separation to yield a long-lived ion pair. Time-resolved

EPR spectroscopy shows that the positive and negative ions move independently within the ordered charge conduit structure. We have shown that solid films of a PDI-DPP-PDI molecule, where DPP is a pyrrole dye, upon solvent-vapor-induced self-ordering show an increase in charge separation lifetime from 340 picosec to 4 microsec, providing important insights into how photo-generated charges escape the Coulomb well in which they are generated within molecular solids. Understanding this phenomenon is critical to developing high performance molecular solar cells. We have demonstrated that bio-inspired hydrogen-bonded guanine-quadruplexes provide an important new platform on which to self-assemble photo-driven charge separation systems, and that cyclic naphthalene diimide (NDI) structures serve as excellent charge accumulators to store multiple electrons to drive reduction catalysts. We have shown that visible-light-absorbing perylene-based electron donors have sufficiently good excited state potentials to provide electrons to Pd-phosphine CO₂ reduction catalysts, thus paving the way for generating photodriven multi-electron sources for driving CO₂ reduction catalysts.

EARLY CAREER: Chemical Control of Charge Trapping and Charge Transfer Processes at the Organic-Inorganic Interface within Quantum Dot-Organic Complexes

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Funding: \$750,000 (2010-2014)

PROGRAM SCOPE

The research program funded through the Early Career Research Award aims to design complexes of colloidal semiconductor nanocrystals, also called quantum dots (QDs), and organic molecules in which the interfacial chemistry controls the electronic structure and dynamics of the excitonic state (photoexcited electron-hole pair) of the QD. The program includes two main projects: (1) investigation of the mechanisms by which organic surfactants control the quantum confinement of excitonic charge carriers, and (2) development of models for electron transfer between QDs and adsorbed molecules as a function of interfacial chemistry. Project (1) explores how organic molecules – in particular phenyldithiocarbamates (PTC) – change the confinement potential for excitonic carriers within QDs, and thereby change the steady state and transient properties of the exciton. The objective of Project (2) is to determine the chemical factors that influence the rates of charge separation and charge recombination across the interfaces between semiconductor nanocrystals and adsorbed (or transiently adsorbed) molecules.

FY 2014 HIGHLIGHTS

Project 1: We showed previously that coordination of PTC ligands to colloidal CdSe, CdS, and PbS QDs decreases the optical bandgaps, E_g , of the QDs by up to 970 meV. These values of ΔE_g are—by more than an order of magnitude in energy—the largest bathochromic shifts achieved for QDs in either the solution or solid phases. Within FY 2014, we have determined the dependence of the degree of delocalization by PTC (and similar molecules, thiophenolates) on their surface coverage on the QD by developing an NMR-based method to count PTC and thiophenolate molecules on the surface of the QD. This measurement is challenging because rigid molecules that adsorb strongly to nanoparticles have no NMR signal. We instead count native ligands that are displaced by adsorption of PTC to infer the number of bound PTC.

We have modeled the dependence of exciton delocalization on surface coverage in order to further clarify the interfacial electronic structure of QD-organic complexes. We have also proven that adsorption of PTC and other exciton-delocalizing molecules increase the probability of absorptive and emissive optical transitions, and thereby increases the photoluminescence quantum yield of the QD.

Project 2: We focused this year on a particular system comprising a di-triphenyldiamine (TPD) molecular donor and a CdS QD acceptor. Selective excitation of TPD, which is linked to the QD through a thiolate group, results in the ultrafast transfer of an electron into the conduction band of the QD. The interesting aspect of this system is that it forms a spin-correlated radical ion pair. The lifetime of the charge separated state in this system depends on the strength of an applied magnetic field. The magnetic field dependence, along with EPR spectra, tell us that the electron on the QD is localized in a surface state and avoids recombination with the hole on TPD by hopping across the surface of the QD.

EARLY CAREER: Design of Efficient Molecular Electrocatalysts for Water and Carbon Dioxide Reduction Using Predictive Models of Thermodynamic Properties

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Funding: \$750,000 (2014-2018)

PROGRAM SCOPE

Hydrogen and reduced carbon compounds have been proposed as ideal candidates for chemical fuels from intermittent renewable energy sources, such as solar. However generation of chemical fuels from electricity requires competent electrocatalysts. The proposed research focuses on developing electrocatalysts for the reduction of water to hydrogen, and carbon dioxide to formate. In heterogeneous catalysis, the Sabatier principle is used to generate volcano curves that describe optimal thermochemical properties for key intermediates that result in peak catalytic activity. In most cases, such as hydrogen production and oxidation, the most favorable metals (Pt, Re, Rh, and Ir) are rare and expensive. Molecular inorganic complexes provide an opportunity to use electronic and steric ligand effects to tune the critical thermodynamic parameters of abundant metals to values comparable to key surface intermediates on precious metals. This principle will be applied to the design of aqueous homogeneous catalysts for the reduction of H₂O and CO₂ optimized to function at specific pH ranges. The critical intermediate in both of these reactions is a metal hydride. The strength of this bond, or hydricity (ΔG^{\ddagger}) dictates the overall thermodynamics of the reduction of H⁺ to H₂ and the sequential reduction of C₁ substrates, such as CO₂, CO, and H₂CO (the latter to CH₃OH). ΔG^{\ddagger} will be systematically measured for a series of first row metal complexes to form predictive models for metal and ligand electronic effects.

FY 2014 HIGHLIGHTS

This project was funded in July 2014. During fiscal year 2014 the initial target complex, a water soluble nickel bis(diphosphine), was synthesized and fully characterized. The hydricity of this complex was measured in water, dimethyl sulfoxide, and acetonitrile. We also determined that this complex is stable in water from pH 1 through 7, and our preliminary electrochemical experiments indicate catalytic proton reduction under these conditions.

DOE National Laboratories

Understanding Roles of Ultrafast and Coherent Electronic and Atomic Motions in Photochemical Reactions

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Tamar Seideman; Northwestern University
Felix Castellano; North Carolina State University
Xiaosong Li; Washington, University of
Students: 2 Postdoctoral Fellow(s), 4 Graduate(s), 0 Undergraduate(s)
Funding: \$900,000 (2014)

PROGRAM SCOPE

This program aims at understanding and investigating roles of coherent electronic and nuclear movements in the photochemistry of transition metal complexes (TMC) which is crucial in solar energy conversion and utilization. The program has three specific objectives. The first objective is to identify, characterize and compute functionally important coherent electronic and nuclear motions in the excited state properties of TMCs with one or multiple metal centers. This part of the program focuses on understanding and characterizing fundamental processes involving the fs dynamics of TMCs including (a) interaction mechanisms for ultrashort laser pulses to produce a coherent superposition of excited states whose properties can be controlled by pulse sequence and shaping, (b) subsequent evolution of the excited states of the TMC's, including electronic state relaxation by nonadiabatic effects and subsequent thermal flow to phonons and solvent, and (c) electronic structure studies and modeling of the measureable properties of the TMC's during and after this time evolution. The second objective is to understand and engineer ultrafast two-electron transfer reactions in chromophore-catalyst-chromophore supramolecular TMC assemblies via control of electronic coupling between the chromophores in the assemblies through the linker bridges or via the photoexcitation pulse sequence. The third objective is to investigate the effect of ultrafast "breathing modes" in nanoparticles on the interfacial electron and energy transfer processes of TMC-nanoparticle hybrid structures. Our focus will be on the properties of the TMCs that are influenced by these phonon modes in nanoparticles. For metal nanoparticles, we expect that plasmon excitation will play an important role, leading both to enhanced absorption and scattering of light, and to a number of secondary processes as time evolves, including hot electron excitation and acoustic phonon excitation.

FY 2014 HIGHLIGHTS

The program started in August, 2014. The research highlight is pending until sufficient results are obtained. By the end of FY2014, the most of key players are all in place. The coming ultrafast X-ray absorption spectroscopy experiments at the Linac Coherent Light Source (LCLS) has been planned in

early 2015, and a series of computations have started on excited state optical and X-ray spectroscopic features. The syntheses of several TMCs have been started.

PECASE: Engineering Principles for the Efficient and Effective Manipulation of Energy and Information at the Nanometer Scale

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Funding: \$50,000 (2014)

PROGRAM SCOPE

In our proposed research we will develop the theory and simulation tools necessary to understand thermodynamics of molecular machines on the nanoscale, where large fluctuations and deviations from equilibrium make traditional approaches problematic. We seek the design principles that will allow us to engineer and customize our own efficient and effective molecular gadgetry. We wish to understand the thermodynamic efficiency of molecular motors, the tradeoff of efficiency with power output, how to determine the optimal thermodynamic processes, and how to engineer machines that can approach these optimal performances. We will do so by building on the recent breakthroughs in non-equilibrium small system thermodynamics discussed in the introduction. We will also draw on a wide range of disciplines, including thermodynamics, statistical mechanics, information theory, quantum optics, computer simulation and statistics, with the aim of uncovering additional theoretical and practical insights into nanothermodynamics.

We specifically wish to understand how to engineer our own effective nanoscale mechanism for highly efficient energy transformation, how to master energy and information on the nanoscale, how to mimic capabilities of biological systems, and how to control and characterize molecules machines far from equilibrium. We currently lack the necessary theoretical guidance on the practical limitations to efficient energy conversion on the molecular scale, and away from thermal equilibrium, and practical guidance as how to design and optimize molecular scale machinery to meet our energy efficiency and engineering goals.

FY 2014 HIGHLIGHTS

- “Time Step Rescaling Recovers Continuous-Time Dynamical Properties for Discrete-Time Langevin Integration of Nonequilibrium Systems” was published in J. Phys. Chem. B, 118, 6466-6474, 2014.
- Invited Talks:
 - Frontiers of Physics and Information Processing, Kyoto University, “Geometry of Thermodynamics & Thermodynamics of Prediction”
 - University of Tokyo, “Molecular Machines, Optimal Response, and the Thermodynamic Cost of Nostalgia”

Primary Processes in Photosynthesis

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Funding: \$557,000 (2014)

PROGRAM SCOPE

The aim of this work is to determine the design principles used by natural photosynthetic systems to harvest solar energy and perform charge separation. The photosynthetic unit is one of the supreme and most elegant examples of nanoscale engineering found in nature. Application of these design principles to the conception of new synthetic solar energy devices holds great promise. Both energy and electron transfer are ultrafast processes and thus require the use of femtosecond spectroscopy for their elucidation. This project focuses on the fundamental processes of energy and electron transfer in natural photosynthesis. New ultrafast nonlinear optical spectroscopies have been developed and combined with new quantum-dynamical theoretical methods to provide new insights into the primary steps of photosynthesis.

FY 2014 HIGHLIGHTS

We revisited a previous study of bacteriopheophytin (H) to bacteriochlorophyll (B) energy transfer in the bacterial photosynthesis reaction center experimentally by refining the two-color peak shift and studying neutral, oxidized reaction centers and a mutant lacking the special pair. We found long-lived (up to 2 ps) oscillatory signals that at long time clearly originate from vibrational wavepackets in the B ground state. We note that the electronic structure and function of the bacterial RC is distinct from typical light harvesting complexes, and estimated coupling constant are significantly larger than in FMO and LHCII complexes. To date, the advantages of multidimensional infrared and electronic spectroscopies have never been combined to directly correlate the electronic and vibrational degrees of freedom simultaneously. We have developed two-dimensional electronic-vibrational spectroscopy and implemented the technique in a partially collinear geometry. This has been a very technically challenging project because of the very small signals arising from electronic and vibrational interactions with samples. We constructed the first structure-based model of energy transfer in photosystem II (PSII). In order to model the large number of pigment molecules present in a supercomplex (as many as 324), a coarse grain model was implemented to cluster chlorophylls into domains, that increases the separation of timescales between inter and intra-domain transfer. Using the complete energy and electron transfer model for $C_2S_2M_2$, we showed that light harvesting in PSII cannot be simplified to a single rate-limiting step. Rather, substantial contributions arise from both excitation diffusion through the antenna pigments and transfer from the antenna to the RC. We have shown that the average timescale of excitation energy capture is linearly dependent on the distance of the excitation from the nearest reaction center.

Chemistry with Near Infrared Photons

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PROGRAM SCOPE

The scope of this project consists of the development of efficient, robust photocatalytic subsystems and complete systems for the synthesis of renewable fuels and chemicals using carbon dioxide and water as starting materials, and sunlight as energy source. All-inorganic oxo-bridged heterobinuclear light absorbers coupled to metal oxide nanoclusters are being developed for accomplishing visible light induced multi-electron catalysis for carbon dioxide reduction and water oxidation, using photodeposition methods for the proper coupling of chromophore and nanocluster catalyst. Structures, charge transfer processes and catalytic mechanisms are elucidated by X-ray spectroscopy, transient optical and time-resolved FT-infrared spectroscopy and atomic resolution imaging. The mechanistic understanding gained from the infrared studies combined with electron transfer investigations of the heterobinuclear charge transfer units by time-resolved optical spectroscopy guide the design of units for improved photocatalytic efficiency under visible and near infrared light. Metal oxide core-shell constructs are being developed for separating the water oxidation catalysis from light absorption and reduction chemistry by a nanoscale silica-based membrane. Synthetic methods have been developed for embedding electron or hole conducting molecular wires into the insulating silica membrane, and proton transmission properties of the silica have been quantified. Emphasis is on tightly controlled electron transport from light absorber to catalyst through the molecular wires, on atomically defined contacts between the components, and on the elucidation of charge transport kinetics and efficiency across the assembly. The long term goal is to close the photocatalytic cycle of carbon dioxide reduction and water oxidation on the nanoscale while achieving product separation on the macroscale.

FY 2014 HIGHLIGHTS

Closing of the photosynthetic cycle of carbon dioxide reduction using water as electron source has been demonstrated with a heterobinuclear ZrOCo light absorber coupled to an Ir oxide nanocluster catalyst anchored on mesoporous silica surfaces. Upon charge transfer excitation of the ZrOCo unit, gaseous carbon dioxide is split to carbon monoxide while the charge transferred to the Ir oxide nanocluster oxidizes water to oxygen. Efficient coupling of the light absorber with the Ir oxide catalyst was accomplished by the development of a photodeposition method for the proper positioning of the nanocluster. A similar photodeposition method was developed for the coupling a cuprous oxide nanocluster catalyst for carbon dioxide reduction to the Zr (or Ti) acceptor center, and efficient multi-electron transfer to the nanocluster and subsequent carbon dioxide reduction was observed. Using our recently developed Co oxide-silica core-shell nanotubes as building blocks of arrays for the photoreduction of carbon dioxide by water under product separation, proton transmission through the silica layer under complete blocking of molecular oxygen was demonstrated. The proton transmission property as function of layer thickness was quantified by electrochemical methods. With embedded electron conducting molecular wires, these silica layers constitute robust artificial photosynthetic membranes for product separation. In order to understand the detailed water oxidation mechanism on the Co oxide (spinel) nanoparticle surface, time-resolved FT-infrared spectroscopy was conducted and two transient surface intermediates observed under reaction conditions. One is a Co(IV) oxo species, the other a superoxide surface intermediate. The temporal behavior of the intermediates revealed the presence of a fast and a slow catalytic site on the Co oxide surface.

Artificial Photosynthesis for Fuel Generation in Solution and at Interfaces

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Funding: \$2,355,000 (2014)

PROGRAM SCOPE

The goal of our research is to gain a fundamental understanding of processes involved in the chemical conversion of solar energy. The long-term storage of solar energy as fuels requires efficient coupling of light absorption, photo-induced electron-transfer processes, and chemical transformations, together with managing proton movement and charge leveling in catalysts.

The effort in subtask 1 entitled "Reductive Half-reactions for Photogeneration of Fuels" consists of: (1) searching for visible-light absorbers (e.g., metal complexes and semiconductors) and coupling them with catalytic processes; (2) avoiding high-energy intermediates through multi-electron/multi-proton processes; (3) using inexpensive metals, or metal complexes that have bio-inspired or non-innocent ligands to achieve low-energy pathways via 2nd-coordination sphere interaction; (4) immobilizing catalysts on electrode or semiconductor surfaces for the highest possible reaction rates and slowest unwanted side reactions; and (5) adopting water as the source of protons and electrons. The utilization of water as a source of protons and electrons for solar-derived fuels requires the concurrent oxidation of water to oxygen.

In subtask 2 entitled "Photo- and Electrochemical Water Oxidation", mechanisms and new catalysts for photo- and electrochemical water oxidation are investigated in addition to efforts (1-4) mentioned above.

FY 2014 HIGHLIGHTS

- Reversible H₂ storage via interconversion of CO₂ and formic acid near room temperature with pH as the 'switch' for controlling the direction of the reaction has been investigated using as catalysts Iridium species with a series of bioinspired ligands. The pH-dependent mechanisms of formic acid dehydrogenation have been elucidated by kinetic isotope effects. Related new cobalt(III) complexes have been prepared and tested for CO₂ hydrogenation.
- A new strategy for the electrocatalytic reduction of CO₂ to CO, using a room-temperature ionic liquid as both the solvent and electrolyte, has resulted in enhanced catalytic activity at lower overpotential than in acetonitrile. When a Re-based catalyst is used, the CO₂ reduction rate constant in the ionic liquid exceeded that in acetonitrile by over an order of magnitude.
- A mononuclear ruthenium(II) complex that contains no water molecule in its primary coordination shell was evaluated as a catalyst for water oxidation. Using a detailed theoretical characterization of the energetics, thermochemistry, and spectroscopic properties of intermediates together with electrochemical and spectroscopic experimental data, a new mechanism for the water oxidation process that involves an unprecedented sequence of seven-coordinate ruthenium complexes as intermediates was elucidated.
- Kinetic isotope effects of novel carbon-to-metal hydrogen atom transfer reactions, in which homolytic cleavage of a C–H bond is accomplished by a photogenerated metal-centered radical, were investigated for the first time. The large primary kinetic isotope effect of 16.8 ± 1.4 observed for hydrogen atom abstraction from xanthenes to an Os radical at 25°C together with the observed

activation energy difference and the preexponential factor ratio suggest a quantum mechanical tunneling mechanism.

- Alternative materials to platinum-based catalysts are required to sustainably produce hydrogen from water at low overpotentials.

Fundamental Investigations of Water Splitting of Model TiO₂ Photocatalysts Doped for Visible Light Absorption

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Funding: \$699,000 (2014)

PROGRAM SCOPE

The goal of this project is to provide new fundamental knowledge regarding complex oxides employed in solar photocatalysis through deeper understanding of interfacial phenomena that impact photocatalytic performance and long-term stability. The need for alternative energy sources has motivated intense searches for new materials capable of efficiently converting sunlight into electrical or chemical energy. To date, a major focus of heterogeneous solar photocatalysis research has been on discovery and optimization of new solar photocatalytic materials guided primarily by bulk material properties (e.g. composition, structure, optical properties and photoconductivity). Unfortunately, the inclusion of interfacial properties is frequently neglected despite the fact that interfaces are the gateways through which solar absorptivity is translated into chemical conversions. Key knowledge gaps exist in the optimization of bulk and interfacial oxide properties that control interfacial electron transfer performance. We employ advanced epitaxy oxide film growth methods, high-level theoretical approaches and modern surface science techniques to provide a combined bulk and interfacial understanding to the field of solar photocatalysis. Focusing on ternary model Fe oxides capable of solar photocatalysis (because of their low cost and high visible light absorptivity), this project is dedicated to preparing well-characterized oxide films and understanding their photochemical properties under similar well-controlled conditions. We also strive to understand how energy is dissipated from interfacial electron transfer events and how such effects contribute to photocorrosion of iron-based oxides. These proposed activities directly address the DOE's mission to promote fundamental understanding of photochemical conversions.

FY 2014 HIGHLIGHTS

The focus of this project in FY14 has been on the growth, characterization and photochemical study of mixed corundum oxides of Fe. Below are highlights from those efforts:

- Growth and characterization of α -(Fe_{1-x}Cr_x)₂O₃ films: We prepare single-crystal corundum films of α -(Fe_{1-x}Cr_x)₂O₃ (0 ≤ x ≤ 1) on α -Al₂O₃(0001) in which the Fe and Cr were homogeneously distributed. High 'x' films were partially strained and O deficient; low 'x' films contained excess O. XPS verified that both cations were 3+. The VB shifted toward the Fermi level for x up to ~0.5 resulting in a decrease in the bandgap observed by optical absorption spectroscopy and

photoconductivity. Alloying Fe_2O_3 with Cr_2O_3 also raised the conducting band minimum, which may reduce the over-potential required for photoelectrochemical water splitting.

- Optical transitions in $\alpha\text{-(Fe}_{1-x}\text{Cr}_x)_2\text{O}_3$ and $\alpha\text{-(Fe}_{1-x}\text{V}_x)_2\text{O}_3$: We calculated the optical properties of $(\text{Fe}_{1-x}\text{Cr}_x)_2\text{O}_3$ using an embedded cluster approach and the time-dependent DFT (TDDFT) method. At $x=0.5$, the bandgap was calculated to be ~ 0.7 eV less than that of pure $\alpha\text{-Fe}_2\text{O}_3$, consistent with experiment. This resulted from two effects: (i) a raised valence band maximum, and (ii) the appearance of $\text{Cr} \Rightarrow \text{Fe } d-d$ transitions (≈ 1.9 eV) in the solid solutions. Spin disorder promoted rehybridization of the O $2p$ and Fe/Cr $3d$ states.
- Photochemistry of a mixed Fe+Cr oxide surface: Underscoring the importance of interfacial properties, we found that the interface of a bulk $\alpha\text{-(Fe}_{.75}\text{Cr}_{.25})_2\text{O}_3(0001)$ film reconstructed in vacuum to a $(\text{Fe}_{.6}\text{Cr}_{.4})_3\text{O}_4(111)$ surface structure. Using NO as a probe, we observed distinct binding behaviors in TPD associated with surface Fe^{3+} , Cr^{3+} , and Fe^{2+} sites. Photoactivity, as gauged by NO photodesorption, revealed rates sensitive to the NO binding site, following the trend: $\text{Fe}^{3+} > \text{Fe}^{2+} > \text{Cr}^{3+}$. The rates were independent of the wavelength in the visible (460 to 630 nm) and showed activity below the absorption threshold of pure $\alpha\text{-Fe}_2\text{O}_3$, as predicted above.

Charge Separation and Escape in Low Dielectric Media

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Funding: \$588,000 (2014)

PROGRAM SCOPE

The efficiency of organic photovoltaic devices to convert solar energy into electricity depends critically on escape of photo-generated electron-hole pairs from their mutual Coulomb field. Experiments are testing the hypothesis that delocalized electrons and holes can escape from each other even in low dielectric constant media such as conjugated polymer films. The experiments are examining how the Coulomb binding is reduced for delocalized charges and how the Marcus inverted region is enhanced for delocalized species. Experiments to measure these proposed effects of delocalization will determine lifetimes and escape yields for delocalized exciplexes and for electron-hole pairs on conjugated polymer chains. We will also study possibly greater charge delocalization in single-walled carbon nanotubes and in films of conjugated polymers. A central experimental tool is pulse radiolysis, which can rapidly inject electrons or holes into delocalized structures. Pulse radiolysis with absorption spectroscopy on sub-microsecond to picosecond timescales utilizes the facilities of the BNL Accelerator Center for Energy Research (ACER). In addition, advances in applying three other diagnostic techniques along with pulse radiolysis are supporting the scientific objectives: 1) transient microwave conductivity, 2) infrared transient absorption to detect delocalized charges, and 3) pulse radiolysis of thick ($\sim 100 \mu\text{m}$) conjugated polymer films.

FY 2014 HIGHLIGHTS

Electrons and holes on pairs of three unit fluorene oligomers, ($\text{F}^{3+}, \text{F}^{3-}$), show lifetimes of ~ 50 ns when created by pulse radiolysis, suggesting that ions in close contact can live unexpectedly long times before

recombination. The slow recombination may be due to delocalization of the charges. Push-pull or DA polymers, like F8BT, having alternating donor and acceptor groups are known to achieve low band gaps and high efficiencies. We have found the expected result that chemical reduction of F8BT produces electrons localized on the BT acceptor groups. But unexpectedly chemical oxidation produces holes delocalized over at least two donor (F8) groups and F8BT shows a substantial mobility in pulse radiolysis transient microwave conductivity (PR TRMC). The PR-TRMC is a new instrument created in collaboration with Rumbles and Reid of the National Renewable Energy Laboratory. Synthesis of three-unit fluorene oligomers having ortho methyl groups showed that large dihedral angles between the fluorenes raise the energies of electrons, holes and triplets moderately, but have a much greater impact on the energies of singlet excited states. This suggests that short diffusion lengths of single excitons in conjugated polymers may be due to the unusual sensitivity of singlets to dihedral angles.

Electron and Photo-Induced Processes for Molecular Energy Conversion

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Funding: \$2,431,000 (2014)

PROGRAM SCOPE

Using complementary techniques of excitation by fast electrons or photons, we investigate ionizing radiation chemistry and fundamental solar energy conversion chemistry, focusing on short-lived species including excited states, radical ions, and free radicals in condensed media from aqueous and organic solvents to ionic liquids. Work on ionic liquids examines fundamental radiation chemistry, properties and reactivity patterns relevant to energy-related applications. The program develops and operates instruments to study short-lived species, at the Accelerator Center for Energy Research (ACER). These include the picosecond Laser Electron Accelerator Facility (LEAF) with advanced nanosecond mid-IR detection based on quantum cascade lasers and optical fiber single-shot detection with time resolution to 15 ps, a 2 MeV electron Van de Graaff and a ^{60}Co source. The resources provide powerful and rare capabilities to several BNL programs and to external collaborators and users in energy research, as well as unique research on biological processes involving free radicals.

FY 2014 HIGHLIGHTS

Extensive efforts yielded dramatic improvements in LEAF's new transient infrared (TRIR) detection system. The new system allowed, for the first time, direct observation of all the intermediates involved in the formation of a Mn-based CO_2 reduction electrocatalyst. It also provided a new view into formation of ion pairs with organic radical ions and a new method to measure association constants. IR-based dosimetry methods have been developed. We also demonstrated that the LEAF TRIR system could follow the radiation-induced polymerization of a vinylimidazolium ionic liquid on timescales from tens of nanoseconds up to minutes by following the bleaching of the vinyl monomer C=C stretch. This result

indicates that the IR detection systems for radiolysis will be extremely useful for studying polymer synthesis and grafting in many different systems. Pulse radiolysis at LEAF has given new insight into the nature of redox potentials and their relation to ion pairing, and the possibility to measure thermodynamic redox potentials in the absence of electrolyte. Ultrafast capture of pre-solvated holes, a previously unknown process in radiation chemistry, discovered recently using LEAF's OFSS detection system, has been found to play an important role in the production of delayed fluorescence, important to basic understanding of radiation chemistry as well as scintillators.

Solar Energy Research Institute for India and the United States (SERIUS)

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Funding: \$1,250,000 (2014)

Jointly funded by the Chemical Sciences, Geosciences, & Biosciences Division and Materials Sciences and Engineering Division

PROGRAM SCOPE

This research consortium, co-led by the Indian Institute of Science-Bangalore and the National Renewable Energy Laboratory, sets out to create an environment for cooperation and innovation "without borders" to develop and ready emerging and revolutionary solar-electricity technologies toward the long-term success of India's Jawaharlal Nehru National Solar Energy Mission and the U.S. DOE SunShot Initiative. SERIUS carries out fundamental and applied research, analysis and assessment, outreach, and workforce development through specific bi-national projects in three research thrusts: (1) Sustainable Photovoltaics (PV) to develop next-generation materials, devices, and advanced manufacturing processes tailored to the needs, environment, and resource availability of India and the US; (2) Multiscale Concentrated Solar Power (CSP) to overcome critical science and engineering challenges for reliable multiscale (including small 25–500 kW) CSP systems; and (3) Solar Energy Integration (SEI) to identify and assess key technical, economic, environmental, and policy barriers, enabling a research agenda for technical readiness in India and of benefit to the U.S. SERIUS has created a bi-national network for fostering new ideas and collaborations to expedite a sustainable industry. SERIUS is developing disruptive technologies through foundational research in PV and CSP to address the critical barriers for solar energy development in India that intersect the grand challenges for solar

energy in the U.S. SERIUS is jointly funded under the Joint Clean Energy Research and Development Center (JCERDC) through the U.S. DOE and the Government of India over a 5-year period (starting October 1, 2012). The Consortium is also supported by cost share from its members. The Consortium comprises 32 partners from India and the U.S.; further information on these organizations and specific SERIUS activities is available on its website: www.SERIUS.org.

FY 2014 HIGHLIGHTS

Photovoltaic Thrust: • Development of new polymers for dye-sensitized solar cells (DSSC) and organic photovoltaics (OPV) based on starting molecule computational analysis, and initial device development and subsequent testing across the team. • Initial CZTS electrodeposition showed correct phase formation without hydrazine on Willow Glass; nanoparticle-based CIGS resulted in meaningful efficiencies. • The electroluminescence technique was developed as a tool to evaluate heterojunction with intrinsic thin layer (HIT) solar cells. Tests on initial 1-cm² and subsequent 25-cm² samples were accomplished. Initial results demonstrate that this can be an important basic diagnostic for HIT and other solar cells. • Developing a comprehensive database for insolation and reliability vs. climate across India to provide a basic understanding of resource availability and failure modes in order to produce mitigation strategies for this significant Indian problem. • Developing an understanding of the dust and soiling problems in India and the development of coatings-based mitigation strategies. • New nano-hybrid encapsulation technology gives very low water vapor transmission rate (WVTR).

Multiscale Concentrated Solar Power Thrust: • Optimization and engineering models for new scalable systems using CO₂-based Brayton (high temperature) and organic-based Rankine cycles (low temperature) have produced new technology-specific designs that are now under construction. • A new turboexpander is being fabricated and will be evaluated in a new test bed for high-temperature Brayton cycle. • A tubular serpentine receiver was designed; CFD model predicts an efficiency > 74%. • New Earth-abundant high-performance reflector and absorber coatings developed. • New low-cost heliostats have been developed at very low capex and are begin tested.

Solar Energy Integration Thrust: • Analysis of policies and techno-economics of grid-connected PV in India Roadmap • Draft Roadmap for Energy Storage for India was developed. • Technology improvement opportunities for PV and CSP thrusts are being defined.

Solar Photoconversion in Molecular, Nanoscale and Semiconductor Systems - Excitons in Molecular and Nanoscale Organic Systems

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Funding: \$984,000 (2014)

PROGRAM SCOPE

This project focuses on novel concepts for harvesting solar energy in molecular, nanoscale and semiconductor systems, with the goal of understanding how to convert efficiently the energy of absorbed photons into electricity, chemicals or fuels. The subtask addresses fundamental studies of light absorption, carrier generation, transport and transfer, and focuses on (1) converting photogenerated excitons to charges in molecular and organic nanoscale systems; (2) studying the photophysics and

photochemistry of excitons in conjugated molecules, polymers, and single-walled carbon nanotubes; and (3) uncovering, through chemical doping and photoexcitation, the mechanisms that govern and control the generation of charges, their transport, and recombination kinetics.

FY 2014 HIGHLIGHTS

- In collaboration with Argonne National laboratory, NREL and Argonne researchers demonstrated charge injection from a semiconducting polymer (P3HT) into single-walled carbon nanotubes (SWCNTs) and observed the spin signature of electrons in SWCNTs. This was the first measurement of a true EPR spin signature of SWCNT electrons. In collaboration with Brookhaven National laboratory, researchers investigated the high-frequency mobility of positive charges (holes) moving along the backbones of an extensive series of fluorene-based oligomers and polymers in benzene using pulse-radiolysis, time-resolved microwave conductivity (PR-TRMC). A one-dimensional diffusion model was used to describe the data that took into account the curvature of the polymer backbone, the length distributions of the polymers, and the possibility of defects along the chain.
- NREL researchers utilized a distinct spectroscopic signature of charges within single-walled carbon nanotubes (SWCNTs), the absorbance of a trion quasiparticle, to measure both the ultrafast photoinduced electron transfer time (τ_{pet}) and yield (ϕ_{pet}) in photoexcited SWCNT-C₆₀ bilayer films. This was the first use of the trion spectroscopic signature to measure ultrafast photoinduced electron transfer in any system, and the first measurement of τ_{pet} at the SWCNT-C₆₀ interface.
- NREL researchers used ultrafast transient absorption (TA) spectroscopy to explore the origin of the high singlet fission (SF) yield in crystalline thin films of 1,3-diphenylisobenzofuran. Spectral fitting of absorption lineshapes indicates that thin films of this model SF compound are composed of two polymorphs, the least stable of which displays very high SF yields. The thermodynamically stable form has very low SF yields, attributed to fast excimer or trap formation that competes with SF. The less stable polymorph undergoes SF with a 10-30 ps time constant and much slower trapping.

Solar Photoconversion in Molecular, Nanoscale and Semiconductor Systems - Interfacial Photochemistry and Catalysis

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Funding: \$1,217,000 (2014)

PROGRAM SCOPE

This thrust combines an integrated approach to understanding and controlling the many, coupled processes involved in converting sunlight into fuel. Efforts focus on understanding interfacial photochemistry and photophysics relevant to both small molecule activation (in particular to solar water splitting) and photoinduced electrical energy generation. Model sub-systems are chosen for their ability to provide insight into the most important aspects of photoconversion. In some cases they may be candidates for complete fuel-forming systems, in other cases, they are designed specifically to answer fundamental questions. Specific areas in the FY14 scope included: (1) General methods for producing and measuring the electronic properties of strained catalytic species in nonequilibrium geometries; (2) Studies of the interfacial photochemistry of thin film III-V semiconductor surfaces to understand the

fundamental processes controlling the mechanisms of surface recombination, photocorrosion and fuel production; (3) Exploring the effects of surface defects, interfacial layers, catalysts, etc. on the interfacial photochemistry that controls charge transport and interfacial charge transfer in nanostructured semiconductors such as Si and metal oxides; (4) Addressing fundamental charge generation, separation, and transport events in lead-halide and related perovskite semiconductors.

FY 2014 HIGHLIGHTS

- The first quantitative measurements of the effect of Mo doping on the electron transport rate in nanoporous Mo:BiVO₄ films were performed. It was determined that these films had an electron diffusion length of 300 nm and a charge separation efficiency of 90% and an 80% absorbed photon-to-current efficiency (at 1.23 V vs. RHE).
- NREL researchers described work exploring the hypothesis that each material possesses a continuum of electrochemical and electrocatalytic properties that can be reversibly tuned by mechanical stress over its elastic range. Stretching Ni oxy-hydroxide-coated stainless steel springs was found to provide only a small elastic strain (~0.1% lattice deformation) but, confirming the hypothesis, had significant and reversible increases in the rates of HER electrocatalysis.
- A novel secondary Pt-assisted etch process was found to bury Pt nanoparticle catalysts deep within the nanoporous surface of “black Si” electrodes. This second etch shifted the onset voltage positively, from +0.25 V to +0.4 V vs. RHE, and reduced the charge-transfer resistance with no performance decrease seen for at least two months. Electrochemical impedance studies revealed that the second etch leads to a considerably smaller interfacial charge-transfer resistance than samples without the additional etch, suggesting that burying the Pt NPs improves the interfacial contact to black Si surface.
- Dye sensitized solar cells were fabricated with the singlet fission molecule 1,3-diphenylisobenzofuran as the sensitizer. The short-circuit photocurrent was shown to vary non-monotonically as a function of the thickness of an intervening zirconia layer. The reduced injection rate from the photoexcited singlet state of DPIBF enabled the relatively slow SF process to occur prior to electron injection. Subsequently, the two triplets born from SF could inject into the TiO₂ support and enhance the photocurrent yield.

Solar Photoconversion in Molecular, Nanoscale and Semiconductor Systems - Quantum Confined Nanocrystals and Nanostructures

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Students: 3 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding: \$1,178,000 (2014)

PROGRAM SCOPE

This project focuses on novel concepts for harvesting solar energy in molecular, nanoscale and semiconductor systems, with the goal of understanding how to convert efficiently the energy of absorbed photons into electricity, chemicals, or fuels. The subtask addresses fundamental studies of light absorption, carrier generation, transport and transfer, and focuses on developing and learning how to incorporate quantized nanostructures into high-efficiency solar harvesting systems elucidating the

factors that control energy flow via excitons and carriers through modifying surface chemistry, inter-nanoparticle coupling, composition, and plasmonic interactions.

FY 2014 HIGHLIGHTS

- NREL researchers used QDs as reactants to produce fused PbSe QD dimers by oriented attachment with up to 50% reaction yield. The spectroscopy of the dimers revealed a size-dependent splitting of the 1st exciton band, and a mechanism of the splitting was proposed. Polarization anisotropy and transient grating measurements indicate that the lowest exciton wavefunction in dimers that is neither fully localized nor delocalized. We also have demonstrated the fusing of two different size QDs into a heterostructure, as well as two different materials (i.e., PbSe/CdSe) via the cation-exchange method. These heterostructures serve as models for QD arrays and may facilitate fast charge separation and reduced Auger recombination.
- A study of Si nanocrystals (NCs) revealed that Si trihydride surface groups are the most kinetically reactive species under both thermal- and radical-initiated hydrosilylation conditions. Importantly, PLQY values were found to be comparable for both the radical-mediated and thermal-initiated routes, demonstrating that the surface is equally well passivated by both techniques. Raman spectroscopy of the Si NCs revealed an asymmetric broadening of the Raman peaks, shown to be a unique signature of resonance between LO phonons and carriers undergoing intraband transitions. The results reveal differences in the density of states between bulk, 1D, and 0D Si that may control carrier relaxation channels. Finally, it was discovered that the absorption cross-section of Si NCs when plotted on a per-Si atom basis is up to 5 times greater than that found for bulk Si. Calculations showed that interface-induced scattering enhances quasi-direct, zero-phonon optical transitions and cause the increase in oscillator strength.
- NREL and CU-Boulder researchers have developed a method to probe spatially varying chemical composition of soft matter systems by use of optically controlled and elastically self-assembled plasmonic nanoantennae.

Hierarchical Photosynthetic Systems

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Funding: \$1,824,000 (2014)

PROGRAM SCOPE

This program investigates fundamental mechanisms for solar energy conversion in natural and artificial photosynthesis. The comparison between natural and artificial photosynthesis is used to resolve fundamental cross-cutting mechanisms for solar energy conversion, and to develop strategies for the design of sustainable photosynthetic systems for solar energy conversion. The program investigates mechanisms for coupling transient excited-states produced by photon absorption in light-absorbing molecules to multiple-electron, proton-coupled fuels catalysis in bio-inspired synthetic assemblies and in

chemically-inspired biohybrid assembly. Modular, bio-inspired light-harvesting-linked-catalyst artificial photosynthetic architectures are developed to investigate design principles found in Nature, while chemically-inspired photosynthetic bio-hybrids are developed as an approach for achieving improved solar photons-to-fuels efficiency in photosynthesis by augmenting photosynthetic architectures with abiotic cofactors that introduce novel photocatalytic function. The two opportunities are linked by shared cross-cutting mechanisms for solar energy conversion. A distinguishing feature of this program is the development and combined use of time-resolved synchrotron x-ray spectroscopy and scattering techniques, ultrafast transient optical techniques, and time-resolved, multi-frequency electron paramagnetic resonance (EPR) analyses for determining ground and excited state structures and function of biomimetic hybrid architectures for solar chemical energy conversion.

FY 2014 HIGHLIGHTS

The development of pump-probe X-ray transient absorption spectroscopy capabilities at beamline 11-IDB of the Advanced Photon Source with sensitivities that allow excited-state solar energy conversion processes to be resolved across a wide range of biological and artificial photosynthetic systems. These included resolution of electronic and geometry changes in excited states formed in both copper diimine complexes photosensitizers in artificial photosynthesis (*Dalton Trans.* 2014 2014,43: 17615) and protein environments using the photo-deligation reactions in myoglobin (*Chem. Sci.*, 2014,5, 4136). These results are significant by establishing advanced techniques for achieving high-resolution transient X-ray absorption fine structure (XAFS) and near-edge (XANES) spectroscopy on photo-active protein and photosynthetic samples with 80 ps time-resolution. New ligand chemistries were developed for assembly of mixed-metal, supramolecular architectures comprised of a light-harvesting ruthenium polypyridyl module linked to a hydrogen-evolving cobalt catalyst. These supramolecular assemblies demonstrated complete metal-to-metal charge transfer in the earliest excited state, duplicating the ultrafast long-range separation found in the earliest excited states in photosynthesis, but implemented in a supramolecular design that directly couples light-absorption with the first reduction step needed for hydrogen-evolving solar catalysis (*PCCP* 2013, 15: 21070). Further, a new mechanism for self-assembly of a photosynthetic-catalyst biohybrid was developed, one that utilized protein-directed delivery of a molecular hydrogen-evolving catalyst to the reducing side of photosystem I for light-driven catalysis, and created a photosynthetic hybrid that generated hydrogen in aqueous media near neutral pH at rates greater than two orders of magnitude faster than comparable artificial systems (*JACS* 2013, 135:13246).

II. MATERIALS SCIENCES AND ENGINEERING DIVISION

Biomolecular Materials

Institutions Receiving Grants

Bioinspired Hierarchical Design of Chiral Mesoscale Liquid Crystalline Assemblies

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Funding: \$750,000 (2014-2017)

PROGRAM SCOPE

Biology uses elastic stresses, defects, chirality and hierarchical design strategies to assemble or create a wide range of functional materials, perhaps best exemplified by the complex functions carried out by meso-structured liquid crystalline cell membranes. This hierarchical organization serves as an amplifier that allows highly localized, nanoscale molecular events to propagate into the meso-scale, resulting in dynamic functional properties of biological systems that have not yet been fully realized in synthetic material designs. We are pursuing a program of research in which we seek to recreate such principles using synthetic liquid crystals (LC) as a versatile platform. We are elucidating new hierarchical design strategies that heavily leverage chirality and topological defects to realize equilibrium and non-equilibrium, dynamic meso-scale phenomena in the context of nano- and micrometer-sized LC droplets containing nanoparticles. Specifically, we are unmasking how equilibrium and dynamical phenomena emerge from hierarchical organizations in responsive, chiral liquid crystalline assemblies. Overall, this research will advance new hierarchical designs of meso-scale materials in which biomimetic principles, including the propagation of events or information over multiple temporal and spatial scales, are enacted in a facile manner. The proposed program of research does not seek to design materials for a particular application, but rather elucidate broad design principles that will be employed in future studies targeted at solving energy-related issues.

FY 2014 HIGHLIGHTS

During fiscal year 2014, we have prepared aqueous dispersions of nano- and micrometer-sized droplets of liquid crystals (LCs), and used them as a platform for the development of bioinspired principles leading to hierarchical meso-scale soft materials. Topological defects were formed within the equilibrium morphology of the LC droplets, thereby enabling systematic, fundamental studies of defects and their use in driving functional assemblies with hierarchical structures at the meso-scale. In the context of this latter goal, progress was achieved on two fronts. First, we demonstrated new hierarchical designs of soft matter by focusing on the role of chirality in LC droplets using cholesteric and blue phase droplets. A wide range of previously predicted (but not experimentally observed) morphologies were characterized in experiments, and unanticipated chiral LC droplet structures were also documented. In

addition, we elucidated the effects of adsorbates on the internal organization of chiral LC droplets. These studies, when combined, have substantially advanced our understanding of the ways in which the elasticity of LCs, topological defects and surface anchoring combine with chirality to give rise to mesoscale organizations within the confines of LC droplets. Both equilibrium and dynamical aspects were explored, with a particular focus on the principles by which molecular phenomena, including chirality, were amplified across space and time to the mesoscale. The second area of progress incorporated an additional level of hierarchical organization and complexity by introducing achiral nanoparticles into the chiral LC systems. We elucidated the interplay of LC and nano/microparticle organizations that occur in the resulting assemblies. The large parameter space and multitude of possible outcomes demanded a concerted computational and experimental program, with computational approaches identifying unanticipated meta-stable organization of nanoparticles.

Harnessing Chemo-mechanical Energy Transduction to Create Systems that Selectively Catch and Release Biomolecules

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Funding: \$435,000 (2014)

PROGRAM SCOPE

Living organisms exhibit a remarkable ability to selectively catch, transport, and release biomolecules. For example, motor proteins bound to microtubules can select, bind and carry specific biomolecules as cargo along the microtubule network. The goal of this program is to develop energy-efficient bioinspired materials that harness conversion of chemical and mechanical energy to perform programmable, selective catch, transport and release of specific biomolecules, with further expansion to catching bacterial and mammalian cells. To emulate the cooperative processes of biomolecular signaling and transport, we devise a new class of integrated materials that combine following synthetic and biological chemo-mechanical “smart” components: 1) stimuli-responsive hydrogels, which undergo a volume change in response to external cue, acting as “muscle” and 2) biologically-specific binding species (such as aptamers) that can reversibly change molecular configuration to bind and release targets upon changes in temperature or pH. In such a system, hydrogel can convert chemical energy into mechanical one by actuating embedded microposts, carrying binding species. When submerged in a bilayer fluid containing a biological mixture, the moving posts bind targets and subsequently transport and release them into a different collecting fluid. This platform provides efficient routes to a nondestructive, sequential ‘detection-and-separation’ of targets from complex biofluids, without the need for expensive tools or high-energy inputs. The studies will lay foundation for designing systems that translate a molecular input into a large-scale motion, enabling programmable ‘catch-release’ of specific biomolecules and cells. The research effort involves a computer modeling component, as well, that utilizes a variety of methodologies, including dissipative particle dynamics (DPD) simulation method, to model the catch-release processes, better understand them, and optimize their energy footprint.

FY 2014 HIGHLIGHTS

We have transformed our previously developed adaptively reconfigurable dynamic material system into an efficient sorting device capable of reversible, dynamic capture and release of unmodified target biomolecules from solution. Our broad effort is aimed at exploring the sorting of different types of objects - from proteins to cells. As a first step, we have integrated a pH-responsive hydrogel with embedded microstructures modified with pH-sensitive aptamers, known to strongly bind to the protein thrombin at physiological pH, and subsequently unfold at lower pH to release it. We have measured the device's capture capacity, sorting efficiency, and demonstrated its robustness in repeated catch-release cycles. In parallel, we developed a theoretical model and performed computer simulations allowing us to gain deeper insight in the catch-release process and the effects of key parameters of the system on the separation process and its efficiency. We also demonstrated isolation of thrombin from human serum, confirming the design's performance in complex media. The work is currently under review in a leading chemistry journal. Next, we have started experiments on sorting leukemia T-lymphoblast cells using newly-designed Bioinspired Aptamer-Loaded Dynamic Systems (BALDS), which incorporate cell-binding aptamers in hydrogel rather than on top of microstructures. Preliminary results have shown the capture of the CCL-119 cells, provided first data on the sorting capacity, efficiency and selectivity, and on the cell viability. Simultaneously, we have utilized DPD simulations to model an array of flexible polymer chains attached to a support. The polymer chains display a conformational change from the hairpin to an unfolded structure with an increase in temperature, which modulates their binding ability. Our current model can reproduce this temperature-triggered effect paving the way to modeling the behavior of the polymer chains attached to the thermo-responsive gel network.

Inducing Artificial Morphogenesis in Soft Synthetic Materials

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Funding: \$142,000 (2014)

PROGRAM SCOPE

In biology, morphogenesis refers to the process that causes an organism to develop its shape. In the proposed studies, we will design synthetic systems that can exhibit a form of "artificial morphogenesis", where three-dimensional microscopic objects actively control their association into macroscopic structures. In effect, we will be devising a Lego set where the individual pieces autonomously come together to form a larger assembly and can dynamically rearrange to perfect their structure. Furthermore, in one of the proposed systems, the individual pieces of our Lego set are soft, deformable objects that can morph into different shapes. Hence, the collective migration and merger of these deformable units can lead to larger-scale objects that exhibit a tremendous variety of morphologies. In effect, we will be developing new methods for engineering the growth, shape and functionality of smart, biomimetic materials. The fundamental issue we are attempting to address through these studies is: to what extent can we drive soft matter to organize or self-organize in a programmable manner? We focus on two distinct systems that offer unique attributes for addressing this question. Namely, the communicating microcapsules that can undergo autonomous motion and thus, could provide ideal candidates for self-organizing, programmable systems. Photo-responsive gels constitute another ideal

system since their shape can be readily manipulated and our preliminary studies have revealed a novel means of using light to organize and combine the individual pieces. By attempting to control the shape and growth of soft materials over a range of length scales, we will be addressing one of the stated grand challenges for DOE-related research. Furthermore, by controlling the structure of these systems, we could achieve unprecedented control over the functionality of the material.

FY 2014 HIGHLIGHTS

A remarkable feature of certain biological species is their ability to dramatically alter their shape in response to environmental cues. We developed a computational model for photo-responsive polymer gels that contain spirobenzopyran (SP) chromophores and showed that these materials can undergo three-dimensional biomimetic shape-changes in non-uniform illumination. The SP moieties are hydrophilic in the dark within acidic aqueous solutions, but become hydrophobic under illumination with blue light. Hence, by incorporating these chromophores into gels, light can be harnessed to control the gel's swelling or shrinking and thereby, dynamically alter the gel's shape. We first validated our model for the SP-functionalized gels by determining the effects of uniform illumination on the temperature-induced volume phase transitions in these materials and showed good agreement between our results and available experimental data. We then demonstrated that these gels can be patterned remotely and reversibly by illuminating the samples through photomasks, and thus, "molded" into a variety of shapes with feature sizes that are on the sub-mm length scale. The same sample can be dynamically remolded into another shape, which could enable a different function. Such processes would have a dramatic effect on manufacturing and sustainability since the same sample could be utilized for multiple applications. Furthermore, we showed that by repeatedly rastering the light source over the sample, the system can be driven to exhibit another biomimetic behavior: sustained, directed motion. The introduction of a temperature gradient provides a means of further controlling this autonomous movement (1). The results point to a robust method for controllably reconfiguring the morphology of soft materials. Beyond a single piece of the gel, our findings also provide guidelines for driving the self-organization of multiple reconfigurable pieces into complex architectures.

Integrating Modeling and Experiments to Design Robust Self-Healing Materials

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Funding:	\$320,000 (2014)

PROGRAM SCOPE

Our goal is to create robust self-healing materials by utilizing predictive computational models and precise macromolecular synthesis. In the prior funding period, we successfully fabricated self-healing coatings based on stars and nanogels that contained disulfide links, which could undergo a rapid degenerative exchange, allowing new bonds to be formed as old bonds were broken. Hence, when the network of nanogel particles was mechanically deformed, the particles quickly rearranged and reshuffled so that the structural integrity of the coating was maintained. In effect, this dynamic behavior prevented the coating from undergoing catastrophic failure. The initially prepared materials employed soft polymers, as self-mending occurred only at temperatures above the glass transition temperature.

Also, a degenerative exchange process via radical means required a constant supply of radicals, UV irradiation and the absence of oxygen. We propose to alleviate the limitations of these first generation samples by preparing materials that can self-heal in visible light and in air. We will also address the healing of harder materials by devising a bi-component system, where a soft matrix is reinforced by harder nanodomains. Furthermore, we will introduce a biologically inspired hierarchy of bonding interactions to improve the overall mechanical properties of the hybrid systems. The creation of strong, hard materials that undergo self-repair in air at ambient conditions constitutes a transformative step. This development will pave the way for creating more energy-efficient, reliable systems and extending the lifespan for a broad range of manufactured devices.

FY 2014 HIGHLIGHTS

We collaborated to develop a hybrid computational model for the behavior of networks of cross-linked polymer-grafted nanoparticles (PGNs). The first report on this work was published in *Soft Matter* in 2013 and was featured on the back cover of the issue. We extended the model to investigate the mechanism of strain recovery and self-healing in these dual cross-linked polymer grafted nanoparticle networks. The individual nanoparticles are composed of a rigid spherical core and a corona of grafted polymers that encompass reactive end groups. With the overlap of the coronas on adjacent particles, the reactive end groups form “permanent” or labile bonds, and thus form a “dual cross-linked” network. (Here, “labile” refers to reactive bonds that can readily break and reform, while “permanent” refers to stronger, less reactive bonds that break but do not reform.) We considered the strain recovery of the material after it is allowed to relax from the application of a tensile force. Notably, the existing labile bonds can break and new bonds can form in the course of deformation. Hence, a damaged material could be “rejuvenated” both in terms of the recovery of strain and the number of bonds, if the relaxation occurs over a sufficiently long time. We showed that this rejuvenation depends on the fraction of permanent bonds, strength of labile bonds, and maximal strain. Specifically, we showed that while an increase in the labile bond energy leads to formation of a tough material, it also leads to delayed strain recovery. Further, we showed that an increase in the fraction of permanent bonds not only enables faster recovery, but also yields improved recovery even after multiple stretch-relaxation cycles. Building on this result, we determined the effect of introducing a small fraction of high-strength connections between the dual cross-linked nanoparticles.

EARLY CAREER: Rigid Biopolymer Nanocrystal Systems for Controlling Multicomponent Nanoparticle Assembly and Orientation in Thin Film Solar Cells

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Funding: \$150,000 (2014)

PROGRAM SCOPE

The project seeks to direct the assembly of nanoparticles into two- and three-dimensional crystals of any desired configuration and crystallographic orientation using tunable DNA interactions. Despite the wealth of nanoscale materials that may benefit many current and future solid state technologies, difficulties in controlling and directing their placement and orientation into desired architectures has led

to significant impediments in their applicability. Biological systems can form such structures using their inherent molecular information as guides to assemble organic and inorganic materials into highly organized structures ordered at multiple length scales. Using bio-inspired strategies, the research will control the two- and three-dimensional arrangement of semiconductor nanocrystals into well-defined orientations and demonstrate that this organization can yield optimal performance over traditional approaches. The particular target applications will be photovoltaics and photocatalysis for fuel production.

FY 2014 HIGHLIGHTS

In the past year, we have succeeded in using DNA for producing close packed nanoparticle thin films by using the DNA-QDs and by promoting interparticle DNA hybridization by use of DNA “linkers”. Because we also wanted to explore the effect of DNA on charge transport through the QD films, we focused on using the p-type DNA conjugated CdTe QDs to build p-n heterojunction based solar cells that consist of ITO/ TiO₂/DNA-CdTe/Au. For the photovoltaic studies, DNA-CdTe QD films composed of different sized nanocrystals was prepared and devices were tested first as a function of QD size and later film thickness. All of the devices from the different sized CdTe QDs showed consistent and reasonable current-voltage characteristics where the V_{oc} values were set around 400mV while the short circuit currents (J_{sc}) showed an increase with the larger QDs. In addition to photovoltaics, we have recently shown that using small molecule linkers or DNA to couple two different photocatalysts could yield a significantly higher amount of H₂ produced directly from water and light as opposed to using a single catalyst alone or simply mixing the two photocatalysts in solution.

Self-Assembly and Self-Replication of Novel Materials from Particles with Specific Recognition

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Funding: \$443,000 (2014)

PROGRAM SCOPE

The goals of our program are to understand, discover, design and control the basic interactions between nanoscopic and microscopic units so that complex self-assembly processes and architectures are enabled. We are particularly interested in specific interactions between particles which potentially allow the design of functional structures involving many different components precisely arranged. To this end we have been using DNA with its specific hybridization only between complementary sequences and particularly DNA origami structures with their breadboard like templates to make both reversible and irreversible bonds. The reversibility results from the strong temperature dependence of the hybridization so that bonds form on cooling through a designed temperature and melt on heating. One of our major accomplishments is to selectively permanently bind some of the hybridized pairs using cinnamate and CNVK incorporated instead of bases on a DNA backbone and UV light. We take as a major challenge for demonstrating complex self-assembly the development of a process whereby a designed information containing structure can be self-replicated and exponentially grow. This would

accomplish something that has previously only been observed in living systems and in a few specific synthetic molecules. It would also have a great impact on nanotechnology since large scale production of nanogenerators, machines, electronics, reactors, sensors etc. could be performed with exponential growth. Further, exponential growth can be used to have different “species” evolve by selection and competition. We have used DNA and origamis to program the design of emulsion droplets and colloids as well as nanoparticles. We can also activate processes using light to heat and melt specific hybridized bonds.

FY 2014 HIGHLIGHTS

Self-Replication and Selective Evolution of DNA Origamis: We have designed a process and a system of DNA origami tiles that exponentially replicate a seed pattern, doubling the copies in each diurnal-like cycle of temperature and UV illumination, producing more than 7 million copies in 24 cycles. We use this system to demonstrate exponential selection: two similarly-growing sub-populations, one with a “red” dye incorporated, the other with a “green” dye, can be controlled by colored light. The light heats one species reducing its replication rate. The progeny of the non-absorbing species replicate preferentially and take over the system. The species selection is enhanced by competition for a resource, critical crosslinking strands required for replication. This addressable selectivity of different constituents in the same solution should be adaptable to the selection and evolution of multi-component nanoscopic-microscopic self-replicating materials.

Reentrant depletion Interactions: The depletion interaction, an attraction between colloidal particles from the entropic pressure of smaller particles, is used extensively in self-assembly. The depletion interaction is temperature independent. A common formulation involves non-adsorbing polymers such as PEO dispersed with micron sized colloidal particles. On the other hand adsorbing polymers universally provide a sticky energetic - enthalpic attraction between particles. Nobelist P. G. de Gennes suggested that the most interesting yet unexplored regime is the crossover from non-adsorbing to adsorbing. He was right! A combination of the two attractive interactions leads to a novel regime in which assembled particles disperse. As temperature is increased there are colloidal crystals which then melt and finally re-aggregate. Our discovery provides a fundamental understanding of the polymer-colloid system and opens new possibilities for colloidal self-assembly, crystal and glass, and controlled viscoelasticity.

Hierarchical Active Matter: From Extensile Bundles to Flowing Gels, Streaming Liquid Crystals and Motile Emulsions

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Funding: \$246,000 (2014)

PROGRAM SCOPE

Active matter is an assembly of microscopic objects, each of which consumes energy to generate continuous dynamics. Interactions between such objects lead to collective emergent properties that are strikingly different from those of conventional materials assembled from inanimate objects. An example of active matter is the biological cytoskeleton that is built from ATP consuming actively propelled molecular motors and other filamentous and other building blocks. Being released from the constraints

of the equilibrium the cytoskeleton exhibits remarkable properties such as motility, rapid shape changes and spontaneous internal flows. Our goal is to create biologically inspired far-from-equilibrium polymeric and liquid crystalline materials from purified biological components. We do not want to reverse-engineer any specific biological process, but rather by starting from the bottom up, to systematically explore a nearly limitless space of functionalities that arise once the materials are released from the tight constraints imposed by the laws of equilibrium statistical mechanics. For example, by incorporating molecular motors into microtubule-based liquid crystals we assemble active liquid crystals, a novel non-equilibrium material that exhibits motile defects, spontaneous flow and self-healing. We seek understanding of soft active matter at multiple levels of hierarchy. At the most fundamental level we are developing optical tweezer based technique to characterize the mechanics and dynamics of extensile bundles, which are the fundamental building blocks of microtubule based soft active matter. At the next level of hierarchy we are characterizing how active bundles assemble into bulk isotropic gels and streaming nematic liquid crystals. Finally, we are also examining how confining active matter leads to novel emergent properties such as directional currents capable to material transport.

FY 2014 HIGHLIGHTS

We highlight two important accomplishments during the past year. First, we have developed a technique to measure the depletion interaction between a pair of microtubule filaments using a method that combines single filament imaging with optical trapping. By quantifying the dependence of filament cohesion on both polymer concentration and solution ionic strength, we demonstrated that the minimal model of depletion, based on the Asakura-Oosawa theory, fails to quantitatively describe the experimental data. By measuring the cohesion strength in two- and three- filament bundles we verified pairwise additivity of the depletion interaction. The described experimental technique can be used to measure pairwise interactions between various biological or synthetic filaments, thus complementing information extracted from bulk osmotic stress experiments. In the second important accomplishment we have discover novel far-from-equilibrium dynamical phases in active liquid crystals. It has been well known that in active nematics a uniformly aligned state is inherently unstable and leads to spontaneous generation of topological defect pairs which stream through the system and later annihilate, yielding a complex, seemingly chaotic dynamical steady-state. The common assumption was that such dynamics destroy any long-range order in active nematics. We have identified emergence of order from this chaos in the form of previously unknown broken-symmetry phases in which the topological defects themselves undergo orientational ordering. So far this experimental observation is not described by any existing theoretical model. As such our quantitative experimental finding should spurn the development of more realistic theoretical models active nematics.

Electromagnetic Interactions in Self-Assembled Metallo-Dielectric Biomaterials

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Funding: \$185,000 (2014)

PROGRAM SCOPE

The proposed work seeks to unveil and take advantage of the self-organization principles encountered in viruses and virus systems in order to design, model, and synthesize novel biomaterials with unique functionalities.

FY 2014 HIGHLIGHTS

Fluorescence emission from multi labeled nucleic acid molecules encapsulated in Brome mosaic virus capsids were examined as a function of macromolecular compactness. A kinetic model relating chain compactness to single-molecule fluorescence emission provided a qualitative description of energy transfer and its dependence on shell compactness. We have found that in a dense multichromophore system the rate of energy transfer should scale with distance more gradually than the rate of the Förster energy transfer between two chromophores. As a proof-of-principle experiment, we have compared predictions from a numerical model for confined diffusive motion with the fluorescence emission from virus-encapsulated and free single RNA molecules decorated with multiple cyanine dyes and encapsulated inside microscopic emulsion droplets. Effective quantum yield per labeled particle depended on the expansion state, in agreement with theoretical predictions.

Semiconductor Nanocrystals as Light Harvesters for Biomimetic Solar Fuel Generation

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Funding: \$221,000 (2014)

PROGRAM SCOPE

This project focuses on use of semiconductor nanocrystals as light absorbing elements of bio-inspired structures for solar fuel generation. II-VI semiconductor nanocrystals are strong absorbers (i.e., have high molar absorptivities when compared to natural light harvesting proteins), and their absorption spectra can be tuned through control of size, shape, and composition. For that reason, they can be synthetically tailored to have optimal properties for particular light-harvesting applications. In this proposal, we focus on photochemical conversion of the absorbed solar photons into chemical bonds to create fuels (i.e., artificial photosynthesis). Fuel-generating reactions are kinetically complex, involving multiple charge transfer steps, and typically require the use of catalysts. In natural photosynthesis, this function is carried out by enzymes. Our aim is understand how the light-harvesting function of nanocrystals can be integrated with catalytic functions of fuel-producing enzymes to create synergistic biohybrid structures that efficiently convert solar photons into fuels. For this 3-year period, we focus on H^+ reduction to H_2 , catalyzed by a hydrogenase enzyme. In collaboration with the Photobiohybrid group at NREL, we have developed nanocrystal-hydrogenase biohybrids that produce H_2 under solar illumination. H_2 generation is governed by charge transfer from photoexcited nanocrystals. We aim to understand the details of kinetics and dynamics of photogenerated charges as they move through the integrated system, and to synthetically tailor nanocrystals to control the efficiencies of the desired charge transfer processes and the overall photochemical efficiency. The expected outcome of this project is a set of design principles for bio-mimetic structures that integrate light harvesting and

catalysis to drive desirable chemical reactions with solar energy. The insights developed in this project are expected to have an impact on solar fuels research.

FY 2014 HIGHLIGHTS

The following was accomplished in FY 2014: (1) We utilized ultrafast transient absorption spectroscopy to measure rates and efficiencies of electron transfer from photoexcited CdS nanorods to hydrogenase (H₂ase). This work was published in the Journal of the American Chemical Society and was highlighted in JACS Spotlights. (2) We started the examination of the effects of nanocrystal surface-capping ligands on nanocrystal-H₂ase electronic coupling and electron transfer dynamics. (3) We started the modeling of electron transfer kinetics to determine intrinsic rate constants for the process. (4) We utilized type-II nanocrystal heterostructures to spatially separate photoexcited electrons and holes and measure the effects of resulting long-lived excited states on H₂ production efficiencies. (5) We synthesized surface-capping ligands that may be resistant to photooxidation from the nanocrystal surface.

Experimental Realization of 'Repair-and-Go' Using Microencapsulation of Nanomaterials

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Students: 1 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding: \$128,126 (2014)

PROGRAM SCOPE

This project supports the investigation of biologically-inspired materials science, and specifically nanoparticulate encapsulation methods geared towards promoting the manipulation of nanoparticles on substrates, as well as facile methods of materials repair. In living systems, the rolling adhesion action of leukocytes enables a probing of tissue of various types, with associated sensing of cues (chemical/biological signals) of healthy versus damaged regions. This project develops artificial leukocytes, focusing especially on emulsion droplets that encapsulate nanoparticles, probe damaged substrates, and respond to those damaged regions by depositing nanoparticles into them. Crucial to the success of the project are polymer designs that specifically recognize damaged regions of substrates and are benign to pristine regions. Such specific recognition of damaged vs pristine areas of structures is adapted to this project using purely synthetic systems and replacing biological signals with materials surface energies.

FY 2014 HIGHLIGHTS

Numerous accomplishments were realized in fiscal year 2014, including: (1) The original concept of 'repair-and-go' using polymer capsules as artificial leukocytes was expanded to include different compositions and sizes of encapsulated nanoparticles. This was a critically important development for realizing mechanical repair of damaged substrates, relying on tailoring interfacial properties and wettability of the nanoparticle, polymer, and surface components. Dynamic mechanical analysis serves as a useful reporter of the modulus and stiffness of materials before and after capsule-based repair processes. (2) The project exploited new theoretically-based literature suggesting that liposomes can act

as 'artificial osteoclasts' by probing substrates for debris, and successfully picking up and carrying the debris off of the substrate and into the exterior media. This project showed that properly functionalized polymer droplets, termed 'osteodroplets', perform just this function - in some cases picking up nanoparticles and inserting them onto the capsule interfacial layer, and in other cases engulfing the nanoparticles into the interior solution phase. These findings are particularly new and exciting since the concept is envisaged to have broad applicability in the context of macromolecular materials science and engineering, and new approaches to self-cleaning and self-healing systems.

EARLY CAREER: Directed Assembly of Hybrid Nanostructures Using Optically Resonant Nanotweezers

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Funding: \$150,000 (2014)

PROGRAM SCOPE

Recently, we have demonstrated how the electromagnetic fields in nanophotonic devices are sufficiently strong that they can be used to physically manipulate biological (nucleic acids & proteins) and non-biological (nanoparticles) materials as small as a few nanometers in size. As is discussed in the proposal, this represents as much as a 100 fold improvement over the state of the art and, I believe, could open up brand new area of materials science in which complex hybrid nanostructures with arbitrary properties and composition can be created at will. In the context of this research I propose a fundamental analytical and experimental study aimed at elucidating the underlying physics behind our new assembly process. Specifically we propose to first develop a series of experimentally validated trapping stability and kinetic models aimed at: determining the conditions under which stable nanoparticle manipulation can be realized and understanding the dynamics of particle release. We will then extend these initial efforts to more complex material systems including gold nanoparticles, quantum dots and carbon nanotubes. Finally we will examine multi-particle effects and demonstrate the assembly of at least one novel nanostructure which cannot be assembled via any other existing technique.

FY 2014 HIGHLIGHTS

In 2014 this DOE funding contributed to the development of an entirely new method of measuring nanomaterial interaction forces using the nanotweezer technology. Briefly, direct measurements of particle-surface interactions are important for characterizing the stability and behavior of colloidal and nanoparticle suspensions. Current techniques are limited in their ability to measure piconewton scale interaction forces on sub-micrometer particles due to signal detection limits and thermal noise. Here we present a new technique for making measurements in this regime which we refer to as Nanophotonic Force Microscopy. Using the DOE funded nanotweezer technology, we generate a strongly localized region of exponentially decaying, near-field, light that allows us to confine small particles close to a surface. From the statistical distribution of the light intensity scattered by the particle we are able to map out the potential well of the trap and directly quantify the repulsive force between the nanoparticle and the surface. We have shown that our technique is not limited by thermal noise and

therefore we are able to resolve interaction forces smaller than 1 pN on particles as small as 100 nm in diameter.

Controlling Structure Formation Pathways in Functional Bio-Hybrid Nanomaterials

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Funding: \$360,000 (2014)

PROGRAM SCOPE

This project aims to understand the structure formation pathways in organic-inorganic hybrid materials in which information transfer from the organic into the inorganic phase is critical to directing the assembly of the composites. Self-assembly of silica nanomaterials directed by small molar mass surfactants is the simplest system of study, both in terms of the organic, as well as the amorphous, inorganic phase. The second system uses synthetic block copolymers to direct the assembly of amorphous calcium phosphate hybrids. The structural complexity of the organic structure-directing agents, as well as the inorganic phase is enhanced over the first system, resulting in an increase in the complexity of the expected chemical pathways. Finally, we are using synthetic/peptide block copolymers to direct the formation of crystalline calcium phosphate bio-hybrids. In this system, we are looking at the effect of peptide sequence, i.e. a significantly increased information transfer from the organic phase, on the crystallization of the calcium phosphate phase. In all three cases, controlling interactions at the interfaces of organic and inorganic materials and elucidating assembly pathways is a central focus. Efforts include synthesis of all organic/inorganic precursors and their composites, as well as in-depth characterization of local, global, and where possible interface structure, of assembly intermediates and final products to elucidate governing principles for structure/shape control in the materials synthesis. When successful, results will provide general guidelines and methodologies for the controlled synthesis of hybrid nanomaterials with increasing complexity offering enormous scientific and technological promise, in areas ranging from energy conversion and storage to drug delivery and bone repair.

FY 2014 HIGHLIGHTS

(1) In our studies of silica nanomaterials, we have developed an inorganic material that changes shape upon exposure to water vapor. After the wetting treatment, the cross-sectional shape of aminated mesoporous silica nanoparticles with hexagonal pore lattice changed from hexagonal to six-angle-star, accompanied by the loss of periodic mesostructural order. NMR spectroscopy of samples after wetting treatment displayed a higher degree of silica condensation, indicating that the shape change was associated with the formation of more siloxane bonds within the silica matrix. A model based on the hexagonal pore lattice and assuming shrinkage due to capillary pressure of water in micropores within the silica walls can account for the observation of preferential shrinkage along the (11) direction relative to the (10) direction of the hexagonal lattice. This work may open a path towards novel stimuli-responsive materials based on inorganic components. (2) We have begun to study pathway complexity in the formation of methylammonium lead iodide perovskites (MAPbI_3), an emerging organic-inorganic hybrid material for photovoltaic devices. We have focused on quantitative analysis of the kinetics of MAPbI_3 crystallization and the role of the lead anion in modulating the formation pathway. To this end,

we have studied, by means of *in situ* synchrotron x-ray scattering, the transformation of a crystalline precursor to MAPbI₃ as a function of the lead salt reagent used in the synthesis. By using well-established kinetics models we extracted activation energies for 4 systems based on different lead salts. Furthermore, detailed analysis of the scattering data as well as kinetic parameters allowed elucidation of precursor compositions. The results provide insights into fundamental parameters that govern perovskite growth and grain coarsening. Part of this work has been accepted for publication in Nature Communications, with an additional two manuscripts under review.

Materials Lessons of Biology: Structure Function Studies of Protein Sequences Involved in Inorganic Organic Composite Material Formation

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Funding: \$270,000 (2014)

PROGRAM SCOPE

This DOE project focuses on families of proteins that inhabit the nacre layer of the mollusk shell, a high-performance composite structure that exhibits fracture-toughening and a mineral assembly process that spans several length scales. These proteins create and guide mineral nanoparticles into organized assemblies and introduce micro, meso, and macroporosities to mineral crystals

FY 2014 HIGHLIGHTS

We have identified five mollusk proteins (PFMG1, AP7, AP24, Pif97, n16) that form protein phases that control the nucleation and organization of mineral nanoparticles, leading to the formation of mesoscale mineral assemblies in solution. Further, each of these proteins becomes incorporated into the growing crystal and introduces porosities or voids within the crystal.

Programmable Dynamic Self-Assembly of DNA Nanostructures

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Funding: \$137,000 (2014)

PROGRAM SCOPE

Biological cells achieve dynamic spatial organization by directing the non-equilibrium self-assembly of molecular materials using the outputs of dynamic molecular circuits. These circuits are comprised of receptors (sensors), signaling cascades and gene networks that compute responses to external inputs. Dynamic changes in the outputs of these networks result in changes in the structure of self-assembled materials. The cytoskeleton is an example of molecular dynamic material presenting this organization.

We aim to build materials inspired by this architecture in which rationally designed nucleic acid (NA) structures are controlled by designed NA circuits with dynamic outputs. NAs are highly programmable polymers; a large number of NA structures and circuits have been previously designed. However, the integration of circuits and structures in a complex material is relatively unexplored. We focus on DNA nanotubes, tubular structures that assemble from tiles (monomers), which can be regarded as artificial microtubules, with the goal of controlling how these tubules assemble, disassemble and organize into higher order structures. We aim to 1) Demonstrate that self-assembly of DNA nanotubes can be controlled by the presence in solution of NA species which induce assembly or disassembly pathways; 2) Program assembly and disassembly of nanotubes using NA circuits, including autonomous circuits such as oscillators; 3) Build integrated sensing, processing, and actuation systems for adaptive NA materials. We are designing materials with the ability to reorganize in response to multiple stimuli, to logically integrate multiple stimuli to produce a single, potentially multistep response. Our research will result in modular, scalable NA-based materials presenting programmable geometries at the nanoscale, which can adapt in complex ways to an expandable array of environmental signals.

FY 2014 HIGHLIGHTS

We designed and characterized nanotubes assembling from DAE-E DNA double crossover tiles. We modified tiles to include binding domains for unique DNA or RNA input species. We designed pathways for isothermal assembly (growth) and disassembly (decay) driven by DNA inputs. We optimized tile design (sequence and length of binding domains) to control these reactions in a range of temperatures between 25 and 37° C. Growth and decay can be induced in several cycles, obtaining nanotubes with length distribution whose mean shifts between 6-8 μm and virtually zero. We have also demonstrated assembly and disassembly pathways triggered by the RNA output of synthetic genes. In the next months, we will direct these growth and decay reactions using an *in vitro* synthetic transcriptional oscillator. To design more complex reconfiguration, we have focused on the organization of nanotubes into higher order structures using DNA seeds and capping devices. We developed methods to control where nanotubes grow and in what patterns. By assembling hierarchical seeds we can build flexible nanotube structures (using floppy linkers, publication in preparation) or rigid superstructures with specific geometries (work in progress). The functionality of these seeds can be altered by NA circuit outputs, making it possible to control material structure using signal processing circuits. To redesign the shape of these complex structures in response to a variety of combinations and intensities of environmental stimuli, we have devised new NA signal processing circuits. We are developing general methods to quantitatively control NA circuits using a large variety of non-nucleic acid inputs, including small molecules and proteins. We have also been developing new kinds of NA circuits that dynamically change their outputs in response to changing inputs. A final thrust of our efforts will be to design and construct NA circuits that enable multistage responses.

Long Range van der Waals-London Dispersion Interactions for Biomolecular and Inorganic Nanoscale Assembly

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Funding: \$181,396 (2014)

PROGRAM SCOPE

Our new and expanded overarching objective is to understand and control all fundamental aspects of long-range interactions in heterogeneous materials on the level of nano- and mesoscale materials, providing a platform for novel materials design, assembly and function. Apart from van der Waals interaction, macromolecular assembly design depends also on the detailed knowledge of direct electrostatic (mono- and multi-polar) and solvent-mediated interactions, that did not feature in our previous proposal. In addition to continuing to advance the van der Waals interaction phenomenology, we now identify three additional methodological and conceptual frameworks. These include electrostatic interactions acting between net-charged molecules, as well as between molecules with a multipolar charge distribution and detailed molecular description of solution environment including solvent mediated interactions. This augmented framework of our proposed research will allow us to cover the mesoscales that are implicit in the long-range interactions driven mesoscale design, spanning both the regime of molecular details and then all the way to macroscopic response functions and theories. Our augmented collaborative and interdisciplinary team, involving experimentalists and theorists from Case Western Reserve University, University of Massachusetts- Amherst, and University of Missouri-Kansas City, is singularly qualified for this extension of the framework of our proposal into the field of macromolecular electrostatic, solvent-mediated structural and van der Waals interactions, their fundamental underpinnings as well as applications. We are in fact pushing forward to set up an 'overarching DOE program', dedicated in its entirety to the fundamental aspects of long-range interactions, not shunning the various materials applications on which it will be firmly based.

FY 2014 HIGHLIGHTS

We continued to investigate van der Waals interactions and began implementing theoretical and experimental method to study the charge regulation under various solution conditions and its effect on the non-isotropic charge distributions, as well as to incorporate the structural solvent-mediated interactions into our theatre of biomolecular and inorganic mesoscale assembly and function. We investigated the effect of changes in the dielectric response of a material, amorphous SiO₂, on the Hamaker coefficient of van der Waals interactions. We formulated the theory of van der Waals-London dispersion interaction between different SWCNTs. We calculated the *ab initio* optical properties of amorphous SiO₂, berlinite aluminum phosphate and 7-2 heterostructure model of type I Collagen. Based on the *ab initio* method, detailed studies of the electronic structure and partial charge of RGD (1FUV) peptide and B-DNA oligonucleotides with various composition and stacking sequence under different solution conditions were carried out. Experimentally-determined UV optical properties of berlinite aluminum phosphate and DNA oligonucleotides show strong correspondence with the theoretical results. Our open-source Gecko-Hamaker software project calculates Hamaker coefficients, interaction free energies, forces and torques using the full Lifshitz theory. It was improved by incorporating the specific advances in theory and computation of long-range interactions. The software has more than 1000 downloads during this research program. In addition to the various theoretical approaches, we initiated experimental techniques to measure and manipulate long-range interactions directly. We set up the modified SAXS-osmotic stress experiments and applied it for DNA/DNA long-range interactions and used the static light scattering-second virial coefficient method to investigate interactions of Bovine Serum Albumin proteins at various solution conditions.

A Hybrid Biological/Organic Half-Cell for Generating Dihydrogen

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

Although a number of solar biohydrogen systems have been developed over the last decade, few attain the electron transfer throughput of oxygenic photosynthesis. Any strategy designed to connect the naturally occurring photosynthetic reaction centers with a non-physiological catalyst is limited by the accessibility of its redox chain, which is largely buried within the membrane-spanning region. Two sites in Photosystem I (PSI) show promise for straightforward manipulation: the membrane-extrinsic PsaC subunit, which harbors the terminal redox cofactors, FA and FB, and the phylloquinones in the binding pockets, A1A and A1B. Extraction of the electron from FB would provide an electron with a favorable redox potential for H₂ production ($E^{\circ} = -580$ mV), while a larger driving force for catalysis would be imparted by extraction from A1A and A1B (E° is -800 mV for A1B and E° is -620 mV for A1A). Our DOE-sponsored work has focused on the development of a hybrid biological/organic photo-electrochemical half-cell, which directly connects the FB cluster of PSI to the distal [4Fe-4S] cluster of an [FeFe]-H₂ase with the use of a molecular wire. This allows electrons to be delivered from the acceptor side of PSI to the catalyst rapidly without the involvement of diffusion chemistry. Our results show that when Cyt c₆ is cross-linked to PSI, the PSI-wire-[FeFe]-H₂ase construct evolves H₂ at a rate of 2885 $\mu\text{moles mg Chl}^{-1} \text{h}^{-1}$, which is equivalent to a throughput of 142 $e^- \text{PS I}^{-1} \text{s}^{-1}$. Placing this in perspective, evolve O₂ at a rate of $\sim 400 \mu\text{moles mg Chl}^{-1} \text{h}^{-1}$, which is equivalent to 47 $e^- \text{RCPSI}^{-1} \text{s}^{-1}$, given a PSI to PSII ratio of 1.8. The three-fold greater electron throughput by this hybrid biological/organic nanoconstruct over *in vivo* oxygenic photosynthesis validates the concept of tethering proteins through their redox cofactors to overcome diffusion-based rate limitations on electron transfer.

FY 2014 HIGHLIGHTS

Illumination of the PSI-wire-H₂ase nanoconstruct with visible light between 400 nm and 700 nm resulted in an average quantum yield of 0.10 to 0.15 molecules of H₂ per photon absorbed. The theoretical quantum yield for H₂ generation in the PSI-wire-H₂ase nanoconstruct is 0.50 molecules of H₂ per photon absorbed. The difference is likely the occurrence of non-productive PSIC13G-1,8-octanedithiol-PSIC13G (PSI-PSI) dimers, which would absorb light without generating H₂. Assuming the thiol-Fe coupling is equally efficient at producing PSI-PSI dimers, the theoretical quantum yield would decrease to 0.167 molecules of H₂ per photon absorbed. This value is close to the range of measured values in the current study. We also showed that the electron can be extracted from an acceptor earlier than the FB cluster. A naphthoquinone-containing molecular wire (1-[15-(3-methyl-1,4-naphthoquinone-2-yl)]pentadecyl disulfide) was synthesized and added to the menB variant, where it occupies both the A1A and A1B sites. When a Pt nanoparticle is attached to the free thiol, H₂ is produced at a rate of 67.3 $\mu\text{mol H}_2 \cdot \text{mg Chl}^{-1} \cdot \text{h}^{-1}$. As expected, no H₂ is produced using wild-type PS I, which does not incorporate the quinone, or in the absence of (NQ(CH₂)₁₅S)₂ or the Pt nanoparticle. Surprisingly, the lifetimes of the forward and reverse electron transfer to and from the FA/FB iron sulfur clusters were the same as in native PS I. This means that that the electrons are not transferred from the quinone in the A1A and A1B

sites directly to the Pt nanoparticle. Instead, the rate of H₂ production depends strongly on the concentration of the sacrificial electron donor cytochrome c6. This eliminates the recombination channel between [FA/FB]⁻ to P700⁺ and allows the electrons to be stored in FA and FB. Over time, the electrons bleed up the electron transfer chain from FA/FB to A1A and A1B through molecular wire to the Pt catalyst, where they generate H₂.

Optical and Electro-Optic Modulation of Biomimetically-Functionalized Nanocarbon Materials

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Funding: \$285,000 (2014)

PROGRAM SCOPE

Light-driven molecular transformations have been long explored for various applications from photorefractives, electro-optics, and energy storage to photodetectors. Natural photo-transduction processes such as vision rely on the cis to trans isomerization of a small molecule “retinal”, which induces conformational changes in the surrounding protein and triggers a cascade of biochemical events culminating in transmission of an electrical impulse through the optic nerve to the brain. Many of these light absorbing molecules found in natural systems are not stable outside their biological environment as they photo-bleach quite easily. However, there are a number of synthetic analogues that can potentially mimic the natural photoconduction process. Among many classes of light switchable molecules, azobenzene molecule, which can reversibly isomerize between trans and cis form by illumination with UV light (trans to cis) and visible light (cis to trans), has been of great interests as the dipole moment can be tuned with chemistry, and are remarkably photochemically stable. In the synthetic world coupling these molecules to known semiconductors can result in an ultrasmall light-driven switching device in solid state which mimics natural phototransduction processes. Our research led to the very first demonstration of an optically active nanotube hybrid material by noncovalent functionalization of SWNT field-effect transistors with an azo-based chromophore. Upon UV illumination, the chromophore underwent a trans-cis isomerization leading to charge redistribution near the nanotube. The resulting change in the local electrostatic environment led to a shift in the threshold voltage and increased the conductivity of the nanotube. Our research is focused on understanding the chromophore/ nanotube interactions and gaining mechanistic insight into the effect photo-switching in the molecule on the nanocarbon electronic properties.

FY 2014 HIGHLIGHTS

Summary of accomplishments: (1) Measured Orientation of a Monolayer of Dipolar Molecules on Graphene from X-ray Absorption Spectroscopy: While second harmonic generation can give the macroscopic polarization of the molecules on the substrate, XAS can provide complementary information by directly probing the orientation of specific molecular orbitals. The element- and bond-specific nature of XAS allows us to look specifically at the most relevant part of the chromophores for determining their orientation. (2) Developed a Mechanistic Understanding for Raman Enhancement of Dipolar Molecules on Graphene: A detailed comparison of wavelength dependent Raman signals and spatial mapping of Raman signal from the chromophore on graphene and on bare SiO₂/Si substrates was

undertaken to elucidate the underlying mechanism for a large enhancement in the Raman signal from the molecule on graphene. TD-DFT studies showed that the electronic structure of DR1P/SLG is significantly modified, resulting in a lower band gap. These suggest that the strong Raman signal is due to the strong interaction of large molecular dipole with graphene. (3) Tested the Dipole Hypothesis by Reversal of Internal Dipole: The ability to shift threshold voltages to either more negative or more positive directions would provide significant design flexibility, offering the potential to engineer electro-optic detectors with zero current flow (and thus reduced power consumption) in both the “off” and the “on” states, in analogy with CMOS electronics. *Ab initio* calculations were used to obtain the structure and dipole moments of these molecules. Publications: “Functionalization of Single-Wall Carbon Nanotubes with Chromophores of Opposite Internal Dipole Orientation.” ACS Appl. Mater. Interfaces 2013, 5, 9355; “Raman Enhancement of a Dipolar Molecule on Graphene.” J. Phys. Chem. C 2014, 118(4), 2077; “Orientation of a Monolayer of Dipolar Molecules on Graphene from X-ray Absorption Spectroscopy.” Langmuir 2014, 30(9).

Phospholipid Vesicles in Materials Science

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Funding: \$235,000 (2014)

PROGRAM SCOPE

This proposal has the objective to develop the science basis needed to deploy phospholipid bilayers as functional materials in energy contexts, specifically to: (1) Develop an integrated molecular-level understanding of what determines their dynamical shape, phase behavior and spatial organization, mainly using a combination of fluorescence microscopy and direct optical measurements of long-range fluctuations that characterize membrane bending stiffness and tension when nanoparticles and other adsorbates to bind; and (2) Develop understanding of their diffusion in crowded environments, which our preliminary measurements suggest to be fundamentally more rapid than traditional solid particles of the same size. While fundamental understanding is the main goal, the knowledge gained from this work can be expected to be employed for rational design of biologically-inspired materials function, as the proposed experiments are generic in scope. The context is that materials science of phospholipid vesicles is largely unexplored, having been dominated by biological and biosensor perspectives, yet is critically needed to fuel energy-related science needs. Some involve laying the science basis for eventual artificial photosynthetic membranes for the protein-based conversion of light into chemical energy. A parallel context is that the prominent role of sieving through the environment, when a vesicle diffuses through a network of neighboring molecules that crowd it, has commonality with solute migration through the flexible meshes of membranes.

FY 2014 HIGHLIGHTS

Our methods of single-molecule visualization with large statistical confidence to quantify the full distribution of behavior have resulted in breakthroughs regarding the phenomenon of polymer entanglement, which is one of the most spectacular, and most energy-focused, aspect of polymer science. These studies focus on single actin filaments (on the one hand) and on single chains of DNA (on

the other hand), the advantage of both these molecules being that their internal conformations can be imaged, molecule by molecule. Regarding actin, a combination of sparse and full fluorescence labeling of entangled actin solutions (filaments 17 μ m long at 1mg/ml concentration) allowed us to probe both filament-scale and local polymer dynamics. Despite the fact that on the coarse filament scale the reptation tube idea of classical polymer physics works well, on local scales comparable to mesh size, local tube width fluctuation becomes important, and the correlation between local transverse constraint (width fluctuations) and accompanying longitudinal dynamics was quantified. Regarding vesicles of lipids and polymers, this has been accompanied by focus on precise control the local environment of vesicles, as well as on the dynamics of vesicle shape transformation, with special attention to the mechanical and chemical responses of lipid vesicles and polymersomes on a level of single-vesicle resolution, enabled by a custom-designed, hydrogel based microfluidic device. Other accomplishments concern extending particle tracking capability in the direction of deep quantitative imaging.

Bioinspired Hydrogen Bonding-Mediated Assembly of Nano-Objects toward Adaptive and Dynamic Materials

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Funding: \$480,000 (2014-2017)

PROGRAM SCOPE

The objective of this project is to investigate new strategies for designing strong, autonomous self-healing materials for potential energy relevant applications. The design of polymeric materials that spontaneously repair mechanical damages would dramatically improve the safety, lifetime, and energy efficiency of many systems. During the previous grant period, our lab has successfully developed a few new strategies for designing autonomously self-healing polymers using both supramolecular and dynamic covalent interactions. A key concept we have proposed is the multiphase self-healing material design that can combine high modulus, toughness, and autonomous self-healing capability. We have shown that this concept is generally applicable to a range of multiphase material systems. Furthermore, we have demonstrated for the first time that olefin metathesis is an extremely efficient dynamic covalent interaction for self-healing purpose. Built upon these successes, we propose the following new studies toward the design of strong, autonomous self-healing polymeric materials: 1) dynamic metal-ligand interactions for multiphase self-healing polymers; 2) combining supermolecular and dynamic covalent interactions for self-healing; and 3) self-healing inorganic-organic nanocomposites.

FY 2014 HIGHLIGHTS

In this year, we have achieved a number of major breakthroughs in designing dynamic/self-healing polymeric materials including: (1) We succeeded in a new design of using dynamic metal-ligand interactions for strong polymeric material able to spontaneously repair itself, without any external help from light, heat, healing agents, or plastizers/solvents (J. Am. Chem. Soc. 2014, 136, 16128–16131). (2) In a fundamental study, we demonstrated for the first time a direct correlation of single molecule properties with bulk mechanical performance for biomimetic design of polymers. The work was published in the Nature Materials (Nat. Mater. 2014, 13, 1055–1062).

Multicomponent Protein Cage Architecture for Photocatalysis

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

The primary goal of the project is to develop protein-templated approaches for the synthesis and directed assembly of semiconductor nanomaterials that are efficient for visible light absorption and hydrogen production. In general, visible-light-driven photocatalysis reactions exhibit low quantum efficiency for solar energy conversion primarily because of materials-related issues and limitations, such as the control of the band gap, band structure, photochemical stability, and available reactive surface area of the photocatalyst. Synthesis of multicomponent hierarchical nano-architectures, consisting of semiconductor nanoparticles (NPs) with desired optical properties fabricated to maximize spatial proximity for optimum electron and energy transfer represents an attractive route for addressing the problem. Virus capsids are highly symmetrical, self-assembling protein cage nanoparticles that exist in a range of sizes and symmetries. Selective deposition of inorganic, by design, at specific locations on virus capsids affords precise control over the size, spacing, and assembly of nanomaterials, resulting in uniform and reproducible nano-architectures. We utilize the self-assembling capabilities of the 420 subunit, 60 nm icosahedral, P22 virus capsid to direct the nucleation, growth, and proximity of a range of component materials. Controlled fabrication on the exterior of the temperature stable shell is achieved by genetically encoding specific binding peptides into an externally exposed loop which is displayed on each of the 420 coat protein subunits. Localization of complimentary materials to the interior of the particle is achieved through the use of scaffolding-fusion proteins. The scaffolding domain drives coat protein polymerization resulting in a coat protein shell surrounding a core of approximately 300 scaffolding/fusion molecules. The fusion domain comprises a peptide which specifically binds the semiconductor material of interest.

FY 2014 HIGHLIGHTS

Plasmonic nanostructures are highly attractive in absorbing visible light and preventing recombination of electron-holes for efficient photocatalysis. A novel synthesis strategy was designed to form core-shell like structure with CdS NPs and Au NPs using genetically engineered P22 templates. In this approach, CdS NPs were confined within the virus-like particle (VLP) via selective peptide sequences on scaffold proteins, prior to nucleation and growth of plasmonic NPs (Au) on the outside coat proteins. The biotemplated Au/CdS nanostructures exhibited significantly enhanced activity for photodegradation of methylene blue as compared to VLPs with only CdS or Au NPs. In another accomplishment, short peptides reported to nucleate the crystallization of TiO₂ in both anatase and rutile forms were genetically fused to the C-terminal 162 residues (141-303) of P22 scaffolding protein. Analytical ultracentrifugation was employed to demonstrate that the fusion proteins re-entered the protein cage. Incubation of these particles with titanium (IV)-bis-ammonium-lactato-dihydroxide (TiBALDH) precursor resulted in the formation of multiple electron-dense NPs contained entirely within the shells. Dissociation of the shells at various times during mineralization allowed us to determine the kinetics of crystal growth and the average size of the NP (2.5 nm). HRTEM demonstrated that the TiO₂ was

crystalline and that the phase (anatase or rutile) corresponded to that expected based on the fused peptide. Under illumination, the particles were capable of generating reducing equivalents as measured by breakdown of methylene blue.

Designing Smart, Responsive Communicating Microcapsules from Polymersomes

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

The continuing goal of this project will be to design motile systems using responsive and adhesive microcapsules that can respond to changes in environmental stimuli and induce collective, smart behavior on length-scales well beyond that of the capsule itself. The general principle that will be employed is particle taxis – or directed motion – in response to nanoparticles or enzymes or analytes that are released from a source capsule in response to light, change in pH, or enzymatic activity. Central to our design are vesicles of various designer chemistries. One such type of vesicle is the polymersome – vesicles whose outer membrane is assembled from block-co-polymers. We have shown that we can make large, uniform populations of polymersomes and have designed these capsules to encapsulate and release active agents such as nanoparticles or molecules in response to stimulation such as light. We also propose to use protein vesicles in which protease cleavable domains have been inserted, and use proteases to release contents on cue, as well as polymer capsules incorporating gold nanorods that release nanoparticles in response to light. In these proposed experiments, we will release encapsulated nanoparticles from source particles, and induce the motion of target particles through haptokinesis (by making a gradient of particles on a surface) or chemokinesis (making a gradient of particles in solution). We have already developed methods for making spatial, ordered arrays of microcapsules using micro-contact printing. Within these ordered arrays, using nanoparticles and surfaces with tailored adhesiveness, and using microfabricated chambers that minimize convection and set the length scale of particle coupling, we will make a direct test of the principles of collective smart particle motion. Furthermore, we include principles of self-propulsion from either thermal or biochemical interactions to make capsules that are motile on designer surfaces.

FY 2014 HIGHLIGHTS

We developed a method for patterning biotinylated polymer vesicles on arrays stamped with avidin, an essential technology for making a communicating array. The patterns allow us to position vesicles with separation distances ranging from 10 to 50 microns (or larger). (Kamat, N.P. *et al.* (2013). *Small*, 9; 2272). Then we showed that these vesicles could be displaced by both soluble biotin as well as particles of different sizes bearing biotin, ranging from 8.6 microns to 33 nanometers. This is an essential step for displacing microcapsules and developing coordinated motion using release from neighboring capsules. These results refute criticisms that avidin-biotin interactions are too strong to permit displacement (Park, S. *et al.*, manuscript in preparation). We measured the materials properties of vesicles made by microfluidics that include a variety of different co-surfactants, including bovine serum albumin and polyvinyl alcohol. These formulations and measurements allow us to determine the best conditions for

making floppy vesicles and hence autonomously motile systems. (Jane, W.-S. in press, Macromolecular Research Communications). We developed a system where by the addition of glucose could lead to the release of contents from vesicles. We encapsulated the enzyme catalase within a vesicle; this enzyme catalyzes the conversion of hydrogen peroxide to water and oxygen radical. We then added glucose and glucose oxidase outside the vesicle. This reaction leads the formation of hydrogen peroxide, which readily permeates the cell membrane. Once it does, it is converted by catalase to oxygen radical, leading to bursting the vesicle and the release of its contents. So, we can coordinate the release of material from vesicles (such as nanoparticles that displace neighboring particles) by the addition of a sugar, ultimately driving the autonomous coordinated motion of capsules through the addition of a sugar. (Jang, W.S. *et al.*, manuscript in preparation).

Surface Mechanical Properties of Bio-Inspired Architectures

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Funding: \$280,000 (2014)

PROGRAM SCOPE

Materials in nature have evolved to form remarkable surfaces with unique surface mechanical properties. These are interesting to the materials scientist because (a) properties are often obtained by manipulation of near-surface architecture, (b) these rely primarily on non-covalent interactions, and (c) combinations difficult to obtain in synthetic materials, such as actively switchable properties and high selectivity, are routinely achieved in nature. The overall goal of our work is to design bioinspired architectures with controllable surface mechanical properties and to understand the surface mechanical properties of compliant materials. In our current work, we have a focus on two problems: (1) The role of surface-tension, solid capillarity, in soft biomaterials Many biomaterials and synthetic biomimetic materials are very compliant compared to conventional engineering materials (e.g., metals and ceramics). Although the role of surface energy is well-known in determining surface mechanical properties such as adhesion and friction, the effect of the equally fundamental surface mechanical property, solid surface tension, has generally been ignored. However, it has become apparent from recent findings that surface tension plays a significant and unexplored role in soft materials. We are studying experimentally and theoretically several phenomena where solid capillarity can play an important and sometimes dominant role, e.g., shape change due to surface tension, resistance to wetting forces, fracture, and adhesive contact. (2) Biomimetic surfaces with highly selective adhesion using shape complementarity There are many examples in nature, ranging from the molecular recognition to millimeter-scale attachment devices, of architectures that obtain highly selective and enhanced adhesion using shape-complementarity. We are studying how some simple designs of shape-complementary surfaces can strongly enhance or reduce adhesion, making it highly selective.

FY 2014 HIGHLIGHTS

(1) Ridge-channel, shape-complementary, surface structuring results in strongly enhanced and highly selective adhesion. We showed that biomimetic ridge-channel surfaces have highly enhanced adhesion (up to a factor of 30) against shape-complementary surfaces and highly attenuated adhesion against

others. We showed that mismatch is accommodated by defects that are effectively screw dislocations. (2) Measuring solid surface tension by placing a liquid drop under a solid thin film. The wetting of solid surfaces by liquid drops is a fundamental phenomenon that, for stiff materials, is governed by the well-known Young's equation for balance of surface energies at the contact line. For compliant materials, the deformation of the material in response to the forces applied by the liquid drop can be quite significant and the resistance to deformation is strongly influenced by solid surface tension. Our work revealed directly the role played by surface tension on a material (PDMS) that is used very widely in research on biomimetic materials. The specific geometry we employed allows one to extract solid surface tensions for materials with stiffness several orders of magnitude greater than done previously. (3) Surface tension of a soft solid flattens surface undulations. Nearly all works on creating biomimetic structures for enhanced and controlled surface mechanical properties rely on creating structured surfaces. In many cases, this is accomplished by some form of molding technique. We have shown how, by exerting forces that flatten and round-off surfaces, surface tension limits our ability to replicate master shapes by molding. To analyze such deformations, we have developed both analytical models as well as computational techniques.

Enzyme-Controlled Mineralization in Biomimetic Microenvironments Formed by Aqueous Phase Separation and Giant Vesicles

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Funding: \$207,000 (2014)

PROGRAM SCOPE

The goal of this project will be to develop and understand materials synthesis in biomimetic microcompartments based on lipid vesicles and aqueous phase separation. Phase separation is common in polymer solutions and provides a means of compartmentalizing reagents and reactions in a biocompatible solvent system that models the macromolecular crowding observed *in vivo*. In such systems local concentrations and diffusion-limited reaction fronts can be controlled and symmetry-breaking can be achieved. We will take advantage of molecular partitioning of solutes between the two phases of an aqueous two-phase system (ATPS) to control local concentrations of enzyme catalysis, metal cations, and other molecules that participate in the reactions. The ATPS will be encapsulated within semipermeable microscale reaction vessels to produce artificial mineralizing vesicles that perform materials synthesis. We anticipate that the approach will be generally applicable to many materials systems including but not limited to those traditionally formed by living organisms. Our initial focus will be on the well-characterized biogenic mineral calcium carbonate, to facilitate interpretation of changes in the process and final products of mineralization related to our approach. The long-term impact of this work will be to enable the design of new materials with desired properties based on understanding and controlling spatial and temporal reactant availability by biomimetic compartmentalization.

FY 2014 HIGHLIGHTS

Semipermeable, size-controlled bioreactors with aqueous macromolecule-rich interiors were assembled by liposome stabilization of an all-aqueous emulsion. This new way to form water-in-water emulsions

enables simultaneous formation of many nearly identical bioreactors capable of maintaining favorable interior composition while allowing substrate entry and product egress. The polymer-rich aqueous interior serves as a model for biological fluids such as cytoplasm where polymers and biomolecules such as nucleic acids are concentrated by equilibrium partitioning and consequently will never “leak” out. A submonolayer of ~100 nm lipid vesicles stabilizes the aqueous/aqueous interface while allowing transport in/out of droplets. Individual vesicles are jammed at the interface and immobile, which makes it possible to form Janus droplets. This work was published in Nature Communications. We are now developing these structures as artificial mineralizing vesicles for enzyme-catalyzed formation of calcium carbonate minerals.

DNA-Grafted Building Blocks Designed to Self-Assemble into Desired Nanostructures

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Funding: \$479,311 (2014)

PROGRAM SCOPE

We develop transformative, computer-based tools to design DNA-grafted colloids (DBB) that will spontaneously assemble into desired crystal structures. Our proposed “Product Design” mode of research runs counter to the Edisonian approach where building blocks are first synthesized, and then examined as to the structures they assemble into. A primary feature of our approach is that we develop hybrid genetic algorithm based methods to replace this trial-and-error methodology with one that can design DBB that will assemble into desired structures. While our model predictions are critically validated against experiments, the more important point is that this new methodology can revolutionize materials design.

FY 2014 HIGHLIGHTS

Our first paper, published in PNAS, focused on the development of the design methodology that is the central focus of the proposal. To date, experimentally it has been found that DNA grafted colloids formed four different structures – CsCl, AlB₂, Cr₃Si and Cs₆C₆₀. This must be viewed in light of the crystal database which suggests that several hundred known crystal structures exist. Our paper has focused on finding regions of parameter space where these other structures may be found, and made several predictions for new structures – for example we suggested that structures such as Cu₅Zn₈ and Pd₅Th₃, among others, could be formed. Experimental verification of these results raised the important question of what the stoichiometry needs to be to observe these structures. That is, do we need to mix colloids in the ratio 5:8 to observe the Cu₅Zn₈ structure, or is the result robust to the chosen stoichiometry. While there are important exceptions, a generally accepted view is that the right stoichiometry of the two building block colloids needs to be mixed to form the desired crystal structure. In a paper under review in PNAS, we combine experiments and theory on a series of DNA-grafted nanoparticles at varying stoichiometries, including non-integer values, to probe this open question. Both experimental results and theoretical calculations reveal stoichiometry as a new parameter that can couple with the

geometries of the building blocks to tune the equilibrium lattice. Theory also shows that phase coexistence between crystal polymorphs can sometimes occur in regions of non-integer stoichiometry. Thus, while stoichiometry can be a powerful handle for direct control of lattice formation, care must be taken in its design and selection to avoid polymorph coexistence. Another variable we have studied in a paper under review in Nature is to use osmotic pressure, specifically through the addition of PEO to the solution, to facilitate crystal morphology transitions.

Biological and Biomimetic Low-Temperature Routes to Materials for Energy Applications

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Funding: \$350,000 (2014)

PROGRAM SCOPE

New materials are needed to significantly improve the efficiencies of energy harnessing, transduction and storage, yet the synthesis of advanced composites and multi-metallic semiconductors with nanostructures optimized for these functions remains poorly understood and even less well controlled. To address this need, we proposed three goals: (1) To further investigate the hierarchical structure of the biologically synthesized silica comprising the skeletal spicules of sponges that we discovered, to better resolve the role and mechanism of templating by the hierarchically assembled Silicatein protein filament in directing the emergent mineral structure simultaneously with its catalytic synthesis. (2) To extend our successful molecular and genetic analyses and engineering of Silicatein, the self-assembling, structure-directing, silica-synthesizing enzyme we discovered and characterized, to better understand and manipulate in this model system the genetically encoded structural determinants of hierarchical self-assembly and the resultant emergent properties of catalysis and templating of semiconductor synthesis, and (3) to use our biologically inspired, low-temperature, kinetically controlled catalytic synthesis method (based on the kinetically controlled synthesis mechanism we discovered in Silicatein) to investigate the relationship between catalysis and templating of inorganic nanocrystal nucleation and growth in model systems optimized for energy applications. The biologically inspired materials synthesis methods we are developing are low-cost, low temperature, and operate without the use of polluting chemicals. In addition to direct applications for improvement of batteries and fuel cells, the broader impact of this research includes a deeper fundamental understanding of the factors governing kinetically controlled synthesis and its control of the emergent nanostructure and performance of a wide range of nanomaterials for energy applications.

FY 2014 HIGHLIGHTS

Based on our genetic engineering enabling further elucidation of the atomic-level mechanisms of catalysis and nanostructural control by the silica-synthesizing enzyme we discovered, we further developed our biologically inspired, low-cost, kinetically controlled method for catalytic nanofabrication of high-power anodes and cathodes for lithium ion batteries and fuel cells. Nanocomposite electrodes made by our bio-inspired, low-temperature catalytic method consist of tin, silicon or platinum nanocrystals uniformly dispersed by catalytic synthesis *in situ* in the pores of highly conductive microparticulate graphite, carbon nanotubes or exceptionally high surface area graphene; these

nanocomposites exhibited electrochemical capacities, power densities and stabilities significantly greater than commercial materials available at that time. Catalytically produced nanocomposite spinel-CNT cathodes for lithium ion batteries produced by this method exhibit high voltage, high capacity and superior cyclability. Thin films of doped barium strontium titanate made by this method offer the prospect of safer batteries via an internal protectant against thermal runaway. Our kinetically controlled catalytic synthesis of nanocomposite electrodes for fuel cells provided access to new combinations of porosity, conductivity and electrochemical hydrogen oxidation facilitating analysis of the relationships between the porous morphologies of the carbon matrices, the sizes of the platinum nanocrystals and their resulting electrochemical activities. Commercially affordable scalability of these materials was developed with continuous production of the nanocrystalline doped barium strontium titanate. In addition, a new approach to the synthesis of complex ternary nanocomposites of silicon, silica and hydrogen silsesquioxane was developed, enabled by the unique advantages offered by our biologically inspired, kinetically controlled, low-temperature catalytic synthesis method.

Electrostatic Driven Self Assembly Design of Functional Nanostructures

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Funding: \$650,000 (2014-2017)

PROGRAM SCOPE

Molecular assemblies with externally controlled mesoscale morphologies offer the opportunity for developing biomimetic systems with tunable functionalities. Of particular interest are assemblies generated via electrostatic interactions, which play a ubiquitous and central role in governing the structure and functionality of bio-mimetic constructs. The focus of this program is to understand and control the coupling of elasticity and electrostatic interactions in multicomponent membranes formed by the co-assembly of cationic and anionic amphiphilic molecules in aqueous solutions and at planar fluid interfaces. This research will delineate the basic principles and experimental strategies for achieving nanoscale control of the intramembrane arrangements of the poly-ionic components, which produce 1D, 2D and 3D mesoscale morphologies, such as ribbons, sheets and vesicles. Environmental inputs, such as solution pH, salt concentration, and salt composition, will be used to tune the inter-molecular electrostatic interactions. Similarly, the inter-molecular van der Waals' interactions will be adjusted by varying the length of the hydrophobic tails. To explore the possibility of generating 2D nanoscale charge patterned surfaces, differences in the shapes and the lengths of the cationic and the anionic amphiphiles will be introduced. Apart from elucidating the coupling between molecular geometries and the subsequent surface heterogeneities, appropriately constructed 2D nanopatterned surfaces may find applications as designer templates for generating ordered nanoparticle arrays for optical and sensing applications.

FY 2014 HIGHLIGHTS

The shape of nanoscale objects influences interaction and determines its functional capabilities. In particular, the unique functions of charged filaments such as filamentous viruses and the cellular cytoskeleton have inspired the design of self-assembled nanofibers for applications in regenerative

medicine, drug delivery, and catalysis. Using SAXS, we studied the assembly of nanofilaments of +1 azobenzene-based amphiphiles. SAXS showed these highly charged nanofilaments of 5.6 nm diameter order into 2D arrays with large inter-fiber spacing of up to 130 nm. Solution concentration and temperature can be adjusted to control the interfiber spacing. The addition of salt destroys crystal packing. We described the crystallization of bundles of filament networks interacting via long-range repulsions in confinement by a phenomenological model and by computer simulations. Two distinct crystallization mechanisms in the short and large screening length regimes were obtained, as well as the phase diagram. Understanding how to generate and control shape by modifying the environmental conditions is of primary importance in designing systems that respond to external clues. We showed that electrostatic interactions can be used to change the equilibrium shape of shells. Uniformly charged shells were found to undergo shape changes, transforming into ellipsoids, discs, and bowls, as the electrolyte concentration is decreased. This electrostatics-based shape design mechanism, regulated by varying properties external to the shell, can be used to build efficient nanocontainers. We further described the buckling of ionic, crystalline vesicles formed by co-assembling amphiphiles with 3+ head groups and -1 head groups by computer simulations at different concentration of cationic and anionic amphiphiles. We found that as the size of the vesicle decreases the shape of the crystalline vesicles changes from higher to lower symmetry (from icosahedron to tetrahedron).

Dynamical Self-Assembly: Constrained Phase Separation and Mesoscale Dynamics in Lipid Membranes

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PROGRAM SCOPE

We have two over-arching objectives for this project. First, we seek to abstract a physical science based understanding of fundamental rules that determine constrained phase separation processes in lipid membranes. Second, our longer-term objective is to translate these physical principles into quantitative design rules for the development of new classes of membrane-based complex materials that exhibit complex, co-operative, and adaptive behavior at the mesoscale. Our approach is primarily experimental; we employ well-defined model membranes including lipid multilamellae, single supported lipid bilayers, and giant unilamellar vesicles) and examine their spontaneous mesoscale organization and dynamic remodeling in response to intrinsic material constraints and selected environmental perturbations. Specifically, we focus on the roles of (1) interfacial (including interbilayer) interactions and hydration repulsion; (2) imposed shapes and curvatures; and (3) mechano-chemical perturbations including adhesion, tension and lipid-specific chemistries. Interrogating these mesoscale dynamic reorganizations in membrane milieu, which arise from molecular considerations, using spatially- and temporally resolved microscopy and spectroscopy methods (fluorescence, ellipsometric, infrared vibrational, x-ray reflectivity, and neutron reflectivity) yield design rules, which we seek to reconstitute in synthetic material systems. Building on our success during the earlier performance periods, we have organized our work into three specific aims: (1) Characterize the mechanism of inter-layer coupling of laterally phase-separated domains in stacked lipid bilayers; (2) Characterize curvature-dependent dynamic reorganization in membrane milieu; and (3) Characterize real-time effects of mechanochemical

perturbations on lateral phase separation in membrane bilayers. The work is performed in partnership with Prof. Sinha (UC San Diego).

FY 2014 HIGHLIGHTS

Toward each of the aims, we have made significant progress during the FY 2014 academic year, which is elaborated in our technical dissemination through nine journal articles and six presentations by the investigators. The most exciting finding of this period is a study published in a recent issue of eLife: "Oscillatory phase separation in giant lipid vesicles induced by transmembrane osmotic differentials," Kamila Oglęcka, Padmini Rangamani, Bo Liedberg, Rachel S Kraut, Atul N Parikh* eLife 3, Art. No. e03695, 2014 (* Corresponding Author). Here we study dynamic self-assembly at mesoscale in closed lipid vesicles. Giant lipid vesicles are closed compartments consisting of semi-permeable shells, which isolate femto- to pico-liter quantities of aqueous core from the bulk. Although water permeates readily across vesicular walls, passive permeation of solutes is hindered. In this study, we show that, when subject to a hypotonic bath, giant vesicles consisting of phase separating lipid mixtures undergo osmotic relaxation exhibiting damped oscillations in phase behavior, which is synchronized with the swell–burst lytic cycles: in the swelled state, osmotic pressure and elevated membrane tension due to the influx of water promote domain formation. During bursting, solute leakage through transient pores relaxes the pressure and tension, replacing the domain texture by a uniform one. This isothermal phase transition—resulting from a well-coordinated sequence of mechanochemical events—suggests a complex emergent behavior allowing synthetic vesicles produced from simple components, namely, water, osmolytes, and lipids to sense and regulate their micro-environment.

Integrating Rhodopsins in H⁺-FETs for Bioinspired Energy Conversion

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Funding: \$285,000 (2014)

PROGRAM SCOPE

Energy transduction at the nanoscale is key for developing ever smaller self-powered biotic- abiotic circuitry. In biological systems, chemical, mechanical, and electromagnetic energy is converted from one form to another using ubiquitous proton gradients. These proton gradients result in proton electrochemical potential differences, referred to as proton motive force (PMF). The proton pump Bacteriorhodopsin is an example. In *Halobacterium Salinarum*, the light energy absorbed from Bacteriorhodopsin is used to pump protons outwards to form a PMF across the membrane. H⁺-ATPase uses this PMF to synthesize ATP. Here, Prof. Rolandi and Prof. Baneyx propose to develop materials and proton (H⁺)- based devices to modulate proton gradients for understanding and exploiting bioinspired energy conversion. This research is enabled by our ability to control proton currents in H⁺-FETs (Rolandi) and express membrane proteins in large quantities in optimized *E. coli* strains (Baneyx). The project objectives are as follows: (1) Express proton-pumping rhodopsins and proteorhodopsins in large quantities in optimized *E. coli* strains and engineer these proteins to selectively bind to proton contacts. (2) Integrate these proteins in solid-state proton conducting transistors with lipid bilayer contacts. (3) Perform proton transport measurements in the resulting devices to evaluate proton-pumping

characteristics (e.g., voltage, current, ΔpH) as a function of light intensity, wavelength, solution pH, and contact protochemical potential. This research will provide a fundamental understanding of H^+ transport in these hybrid devices. This understanding can then be used to develop rhodopsin-powered circuitry and exploit other aspects of proton based bioinspired energy conversion including chemical energy (ATPase) and mechanical energy (bacteria flagella).

FY 2014 HIGHLIGHTS

During the first year of this grant we focused on the components that will be used in year 2 to assemble HdtR onto the protonic devices to perform measurements. (1) Measurement and Simulation of H^+ injection and depletion from PdH_x contact. To characterize the charge injection characteristics of PdH_x contacts, we integrate PdH_x with the well-known proton conductor (Nafion) and measure transient behavior. (2) Measurement of PdH_x Nernst potential as a function of x and pH. The study of the PdH potential was carried out in an open-circuit measurement. (3) Formation of Lipid Bilayers liposomes for integration onto Pd. The formation of Dioleoylphosphatidyl-Choline (DOPC) liposomes has been confirmed through Dynamic Light Scattering (DLS) measurements. (4) Construction of a Pd-binding derivative of HtdR. (5) Pd_4 -HtdR is expressed in a functional form in the *E. coli* membrane.

Miniaturized Hybrid Materials Inspired by Nature

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Funding: \$315,000 (2014)

PROGRAM SCOPE

The objectives of our research program is to develop a scientific understanding of higher-order-assembly in charged biomolecular materials, which may be near equilibrium, in kinetically trapped states (e.g. in environmentally responsive biomolecular assemblies), or out-of-equilibrium. Current focus includes polyampholyte directed assembly of filamentous proteins and polyelectrolyte directed assembly of oppositely charged membranes. Our program also involves developing an understanding of the influence of shape, in environmentally-responsive tunable bio-macromolecular materials systems, on dynamical assembly. Both the building blocks and their directed assembly may contribute important functional properties to the resulting biomimetic materials on different length scales. A strategy that we use to achieve our aims is to design biomimetic materials inspired by complex cellular assemblies, which operate under dissipative conditions. Bio-macromolecules studied in this program include dynamical filamentous proteins, including neurofilaments (NFs) and microtubules, which assemble as a result of electrostatic interactions mediated by unstructured bio-polyampholytes (e.g. the polyampholytic sidearms of NFs and the unstructured microtubule-associated-proteins). The results should aid in the development of nanoscale and micron scale biomimetic materials with potential applications including as templates for nanostructures and chemical encapsulation systems. The projects utilize the broad spectrum of expertise of the PI and the two co-PIs in biomolecular self-assembling methods, synchrotron x-ray scattering, electron and optical microscopy characterization techniques, the

application of the small-angle x-ray scattering (SAXS)-osmotic pressure technique for direct force measurements, and custom organic/polymer synthesis and purification of biological molecules.

FY 2014 HIGHLIGHTS

“Protein Tubule Inversion Triggered by a Molecular Switch: A New Paradigm for Nanoscale Assembly”, our recent study, which appeared as an article in Nature Materials, describes the discovery of a highly charged molecular switch triggering the disassembly of a bundle of microtubules followed by re-assembly into inverted tubulin tubules, which expose the inner surface of the original microtubules [1]. Synchrotron small-angle-x-ray-scattering and electron microscopy uncovered the pathway of the tubule inversion process revealing a straight-to-curved shape transition of protofilaments comprising the precursor microtubule wall. The scientific discovery opens the path for a new paradigm for nanoscale assembly, which incorporates building blocks with a pre-programmed and triggerable shape evolving property (in principal applicable to a range of enzymes with inherent coded properties). The use of encoded building blocks enables trigger-ready assemblies, which disassemble on demand and reassemble shape-remodeled building blocks into a new form of matter with different function resulting from the evolved structure. The study was further highlighted in a Perspectives article in Science [2]. 1. Ojeda-Lopez, M. A.; Needleman, D. J.; Song, C.; Ginsburg, A.; Kohl, P.; Li, Y.; Miller, H. P.; Wilson, L.; Raviv, U.; Choi, M. C.; Safinya, C. R.: Transformation of taxol-stabilized microtubules into inverted tubulin tubules triggered by a tubulin conformation switch. Nature Materials 2014, 13, 195-203. DOI: 10.1038/NMAT3858. 2. Mark J. Stevens: How shape affects microtubule and nanoparticle assembly, Science 2014, 343, 981-982. DOI: 10.1126/science.1250827. (Perspectives Article)

EARLY CAREER: Assembling Microorganisms into Energy Converting Materials

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Funding: \$150,000 (2014)

PROGRAM SCOPE

This project integrates microorganisms capable of reversible energy transduction in response to changing relative humidity with non-biological materials to create hybrid energy conversion systems. While plants and many other biological organisms have developed structures that are extraordinarily effective in converting changes in relative humidity into mechanical energy, engineered energy transduction systems rarely take advantage of this powerful phenomenon. Owing to their micrometer-scale dimensions, bacterial spores are amenable to integration into macroscopic structures with desired micro-architectures through directed or self-assembly. So, the objective is to create robust and scalable energy conversion materials using bacterial spores as the key biomolecular material responsible for energy conversion. A suite of experimental platforms including atomic force microscopy and micro-electromechanical systems is being used to investigate how to assemble hybrid spore-rubber latex structures that efficiently generate electricity by converting energy from evaporation of water and, how the interaction between water and spore nanostructure imposes limits on energy conversion. Progress can provide opportunities to tap into new forms of renewable energy and environmentally friendly energy storage.

FY 2014 HIGHLIGHTS

We have developed an experimental setup to measure maximum strains and energy densities of individual bacterial spores in response to changes in relative humidity. We also developed a model to better estimate energy density using contact mechanics principles. We studied two different spore species. Our study showed that the energy density of *Bacillus subtilis* is more than 10 MJ m^{-3} , which is two orders of magnitude higher than that of synthetic water-responsive materials. In addition, certain genetic alterations can approximately double the energy density over the wild type. We found that the energy densities of spores also exceed typical values reported for materials frequently used or studied in the context of actuators and stimuli-responsive materials. To demonstrate a potential application of spore-based stimuli-responsive materials, we created a centimeter scale actuator, which can grab and release objects on demand.

Biopolymers Containing Unnatural Building Blocks

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Funding: \$365,000 (2014)

PROGRAM SCOPE

Chemists have exquisite control over the structures of small molecules. However, our ability to control the structures of biological polymers such as proteins and nucleic acids is far more limited. Although it is possible to manipulate protein structures by selective chemical modification and by site directed mutagenesis, we are in general limited by the chemical functionality contained within the canonical twenty amino acid building blocks. For many applications of proteins to problems in energy, the environment or materials science, additional building blocks would be desirable and in many cases essential. To overcome this biological limitation we have developed a method that allows unnatural amino acids, beyond the common twenty, to be genetically encoded in bacteria, yeast and mammalian cells with high fidelity and good yields. Previously, amino acids with novel chemical and photochemical properties, metal ion binding amino acids, and a variety of biophysical probes were genetically encoded. Here we propose to begin to develop approaches to use these new chemistries to selectively modify the structures of protein to generate new functions, and to begin to create new classes of template unnatural biopolymers of defined length and sequence. This work should provide the scientific community powerful new tools to manipulate the properties of proteins in ways currently not possible for energy and materials related applications.

FY 2014 HIGHLIGHTS

We have made significant progress toward this goal of using the templated ribosomal biosynthetic machinery of nature to make unnatural biopolymers. A family of orthogonal nonsense and frameshift suppressor tRNA/aminoacyl-tRNA synthetase (tRNA/aaRS) pairs has been evolved that efficiently incorporate multiple noncanonical amino acid building blocks into proteins. These orthogonal tRNA/aaRS pairs also allow us to simultaneously insert two distinct noncanonical amino acids efficiently into a single polypeptide chain. In addition we have demonstrated that in a TAG codon genomically

deleted strain of *Escherichia coli* which is devoid of the amber stop codon, one can use unique four base suppressor tRNAs to insert amino acids with novel chemical and physical properties into proteins. Furthermore to further expand the range of unnatural building blocks that one can insert into biopolymers using this technology we have evolved a tryptophanyl-tRNA synthetase that genetically encodes a number of novel aromatic amino acids. Finally we have demonstrated that the ability to generate polypeptides with an expanded set of building blocks allows one to evolve novel metal ion binding sites in proteins. This work may afford a strategy for the generation of metal ion binding motifs with novel catalytic or regulatory properties.

Fabrication and Assembly of Robust, Water-Soluble Molecular Interconnects via Encoded Hybridization

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Funding: \$445,000 (2014-2017)

PROGRAM SCOPE

Nucleic acids present the most versatile class of materials for producing nanostructures to date and, through careful consideration of their residue sequence, can be designed to self-assemble via the hybridization of complementary strands into arbitrary structures with nanometer precision. Additionally, the biological origin of nucleic acids enables oligomeric sequences to be readily enzymatically replicated. Unfortunately, the versatility of nucleic acids as construction materials is tempered by the thermal and mechanical instability of the assembled nanostructures, attributable to the weakness of the hydrogen bonds holding the strands together. The substitution of the canonical nucleic acid base pairs with covalent-based pairs would preclude this instability and yield a unique and powerful nanofabrication strategy wherein the complex, sequence-directed assembly of nucleic acids is combined with the strength of covalent bonds. Moreover, the exact monomer positioning resulting from strong, reversible, covalent interactions between sequence-specific oligomeric templates and complementary monomers enables multi-generational, high fidelity replication and amplification of oligomeric sequences. As the utilization of covalent-based pairs necessarily prevents the prospect of enzymatic amplification of the synthesized oligomers, the nucleic acid backbone can also be replaced without considering its enzyme compatibility. Although nucleic acids exhibit poor long-range electrical conductivity, oligomers incorporating an electron-delocalized backbone would afford excellent electron transport. This research involves the utilization of dynamic covalent bonds to mediate the assembly of complementary oligomers, and the semi-conservative replication of these oligomeric sequences, enabling the deterministic assembly of branched nanostructures constructed from robust, electron-conducting interconnections that can be exponentially amplified via repeated duplication.

FY 2014 HIGHLIGHTS

Upon synthesis, purification, and deprotection, we examined the dynamic covalent hybridization of short, aldehyde- and amine-bearing peptoid oligomers in the first period of this research. Reactions of trialdehyde/triamine and tetraaldehyde/tetraamine exclusively afforded the corresponding tri- and tetramer hybrids, respectively. Approaches to achieve hybridization registry between larger complementary oligomers and polymers have long been challenging owing to kinetic trapping, even for

those employing non-covalent interactions. However, cross-reactions of tetraaldehyde/triamine and trialdehyde/tetraamine both yielded least-common-multiple (i.e., 3×4) vernier dodecamer hybrids, providing a facile path for achieving otherwise unattainable hybridization lengths. Additionally, we are currently examining approaches to incorporate both aldehyde- and amine-based dynamic covalent pendant groups on oligomers whilst avoiding premature deprotection which would lead to uncontrolled inter-oligomer cross-linking and impede oligomer purification efforts. To this end, we have developed pendant groups that can be deprotected *in situ* upon ultraviolet irradiation.

Self Assembly & Self-Repair of Novel Photosynthetic Reaction Center/Single Walled Carbon Nanotube Complexes for Solar Energy Conversion

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

Nature continually develops and maintains an infrastructure for light harvesting and energy storage using the self-assembly of photosynthetic protein complexes coupled with mechanisms of repair and replacement of active components. The goal of this project is to continue to study and develop synthetic analogs to natural self assembly and self repair processes in working photoelectrochemical and photovoltaic cells. Previously, we extended these concepts to develop the first synthetic photoelectrochemical complex capable of mimicking key elements of this self-repair cycle (Nature Chemistry, 2010). We found that phospholipids, an amphipathic apolipoprotein (membrane scaffold protein; MSP), single-walled carbon nanotubes (SWNT), a photosynthetic reaction center (RC) isolated from the purple bacterium, *Rhodobacter sphaeroides* all spontaneously assemble into a specific configuration, enabling a photoelectrochemical cell capable of self repair. In this current work, the project will explore two additional topics: energy transfer to biological chromophores and the study of exciton antenna structures. Biological chromophores have an advantage in that they can be directly produced by known biological infrastructure, forming an important basis for self repair. Carbon based antenna structures are a new invention of the Strano laboratory at MIT (solar funnels, Nature Materials, 2010) that allow us to tune and direct excitation to specific reaction centers, giving us the ability to control wavelength and the spatial concentration of excitations. The project will invent several example systems capable of self repair, particularly using nano- and bio-technology interfaces. We also intend to extend our modeling of exciton diffusion and reaction in such systems using Kinetic Monte Carlo methods.

FY 2014 HIGHLIGHTS

From 2014, we published our first work on Plant Nanobionics in Nature Materials, starting a new field of nanoparticle modification of living plants. A press release is below: <http://newsoffice.mit.edu/2014/bionic-plants>

Nanoengineering of Complex Materials

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Funding: \$450,000 (2014)

PROGRAM SCOPE

Our research program is based on complex materials derived from functional nanostructures that emerge as a result of self-assembly of organic molecules. The self-assembly processes can be directed by external forces or can be encoded in the molecules themselves by exploiting chemical reactions involving organic or inorganic substances. The first fundamental objective is to further develop the supramolecular science necessary to design molecules for nanostructure synthesis and function. A second objective is to integrate the synchronized templating of organic and inorganic phases to understand phenomena such as epitaxy on nanostructures and nanoscale confinement of chemical reactions. Self-assembly and templation are two fundamental phenomena used intensely in biological systems for the control of function over many length scales. It is our opinion that both need to be understood deeply to advance materials chemistry over the next few decades. From a functional standpoint, we are interested in new structural concepts in nanoengineered materials for capturing, transducing, and storing energy. We are also interested in enzyme mimics for catalysis and in the design of biomolecular structures to control cell behavior for biosynthesis. Fundamentally, we hope to use the self-assembly strategies that we develop to control and exploit the properties of the resulting bulk materials. Our longer-term goals include development of applications of these nanostructured materials to solar energy conversion, electronic and ionic conductivity, and energy storage.

FY 2014 HIGHLIGHTS

In our project on supramolecular interactions for photovoltaic function, the objective is to use hydrogen bonding to direct the assembly of molecules on an active layer. We designed a family of asymmetric donors containing diketopyrrolopyrrole groups. Since the synthesis of asymmetric molecules is complicated, we switched to a symmetric design. Initial testing of the new symmetric design revealed an improvement on open circuit voltage, but solubility remains a challenge. Going forward, we will keep the symmetric design, but try to design molecules with additional solubilizing groups that do not compromise the electronic properties. Our research into dye sensitized solar cells with a lamellar hybrid organic-inorganic system showed that our initially synthesized dyes did not provide efficient devices. We are now developing new hybrid systems based on electrodeposited molybdenum sulfide-chromophore hybrids for photocatalytic hydrogen production and new, lead-free perovskite systems for solar cells. In our work on supercapacitor and battery electrodes, we have successfully optimized conditions for homogeneous electrodeposition of lamellar surfactant-Co(OH)₂ supercapacitor electrodes and characterized the nanostructure with grazing incidence x-ray scattering (GIXS) and traditional XRD. The electrochemical performance was measured using galvanostatic charge-discharge cycling and cyclic voltammetry. Current efforts include incorporating crosslinking surfactants for improved structural stability during cycling. We have designed and characterized a charge transfer complex that forms nanostructures with alternating electron donor/acceptor functionality. In our newest syntheses, we

have altered the molecular design to improve solubility in organic solvents. We also designed two molecules that incorporate either short peptide or sugar moieties.

Chemically Directed Self-Assembly of Protein Superstructures and Construction of Tunable Redox Functionalities in their Interfaces

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Funding: \$240,000 (2014)

PROGRAM SCOPE

The stated objectives of this project are: 1) To elucidate and control the bottom-up assembly of 0-, 1-, 2- and 3D nanoscale protein superstructures/arrays, and to functionalize them toward energy-related applications. 2) To construct redox-active copper centers in the interfaces of protein superstructures. These goals combined will lead to the chemically controllable self-assembly of well-ordered superstructures under ambient conditions that will be used for light-harvesting and redox catalysis. These structures also will provide a framework for a fundamental understanding of protein self-assembly as well as crystal nucleation and growth.

FY 2014 HIGHLIGHTS

We have made excellent progress in the past year on several fronts, both in terms of building structural complexity and diversity using proteins as synthons for self-assembled systems and in terms of controlling metal reactivity within these assemblies. Excitingly, entirely new research areas and possibilities (related to Biomaterials) emerged from our recent studies, which we had not foreseen when we were formulating our plans for 2013-2015. These include: 1) Construction of *de novo* helical protein nanotubes with tunable diameters, 2) Metal-mediated assembly of 2- and 3D crystalline protein lattices with novel protein building blocks and new bonding strategies, 3) Programmable assembly of DNA-protein hybrids, 4) Construction of protein assemblies with redox-active Cu centers.

Self-Assembly of PI-Conjugated Peptides in Aqueous Environments Leading to Energy-Transporting Bioelectrical Nanostructures

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Funding: \$270,000 (2014)

PROGRAM SCOPE

The realization of new supramolecular pi-conjugated organic structures as driven by peptide-based self-assembly will offer a new approach to interface with the biotic environment. Previously, we developed pi-conjugated peptides that undergo supramolecular self-assembly into one-dimensional (1-D) organic electronic nanomaterials under benign aqueous conditions. The intermolecular interactions among the pi-conjugated organic segments within these nanomaterials lead to defined perturbations of their optoelectronic properties and yield nanoscale conduits that support energy transport within individual nanostructures and throughout bulk macroscopic collections of nanomaterials. Our objectives for this project are to construct and study biomimetic electronic materials for energy-related technology where peptide-driven self-assembly enhances pi-stacking within nanostructured biomaterials. This project entails synthesis of new pi-electron units to embed within self assembling peptides, detailed characterization and molecular modeling of the resulting nanomaterial aggregates, exploration of the surface chemistry presented by these nanostructures as relevant for the development of optoelectronic interaction with cells or other biotic systems and development of new assembly paradigms leading to heterogeneous electronic properties (i.e. gradients and localized electric fields) within the nanomaterials. Collaborative molecular modeling and simulation closely integrated with experimental synthesis and characterization will reveal molecularly-detailed structures and assembly mechanisms to rationalize experimental observations, and present molecular-level guidance to inform peptide design. This research will lead to the continued development of a powerful materials set capable of making connections between nanoscale electronic materials and macroscopic bulk interfaces, be they those of a cell, a protein or a device.

FY 2014 HIGHLIGHTS

Research over the past year has advanced all of the major project aims. We synthesized peptidic nanostructures based on 2-D “graphitic” subunits and new donor-acceptor constructs capable of directed energy migration both lateral to and along the nanowire conjugation axis. We finalized and published studies related to the variation of peptide sequence and resulting impacts on photophysical properties. We investigated the capability of nanowire assemblies to transmit voltage and current by using them in two different functional parts of field effect transistors (FETs), as well as by simple sheet resistance measurements. Sequence composition impacted the magnitude of the electrical conductivities which were also higher than a control nanowire with no conjugated core. These conductive nanowires were effective in transmitting gate voltage to the gate dielectric of an organic FET. Both hydrocarbon and hydroxylated dielectric materials were used in these devices. Separately, we compared various nanowires as semiconductors in FETs with silicon-silicon oxide gates. The most important finding is that the control nanowire did not show a field effect when used as a semiconductor, while many other nanowires, with conjugated cores, did so. We have developed a coarse-grained solvent-free model of peptide assembly tuned against fully atomistic, explicit solvent simulations to understand monomer and dimer behaviors. This model provides access to assembly time and length scales inaccessible to the atomistic molecular dynamics, enabling us to simulate the assembly of hundreds of peptide monomers for hundreds of nanoseconds. Our results suggest the existence of two time scales for assembly: a rapid annealing phase where monomers aggregate into barrel-like groups of ~5 peptides, and a slow ripening phase wherein these barrels coalesce into larger ribbons and sheets. A manuscript is in preparation to be submitted early in the new year.

Dynamic Self-Assembly, Emergence, and Complexity

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Funding: \$900,000 (2014-2017)

PROGRAM SCOPE

This program focuses on the development of two areas. Both are dissipative systems. i) Biomimetic Actuators. We are studying the fundamental materials science of soft actuators and soft machines—that is, devices fabricated predominantly in elastomers and flexible sheets—under actuation (primarily by pressurization with gas). The model “machines” we are characterizing share with living systems an organization around soft materials; the mechanism of actuation of these “machines” (by muscle in the case of animals; by pneumatics in our biomimetic systems) are mechanistically different, but functionally similar. As with living systems, these biomimetic, but non-living systems have the remarkable property of displaying non-linearities in actuation (e.g., stretching or bending) that allow them to substitute the non-linear properties of the materials for sensors and controls: that is, the materials allow the devices to carry out complex functions such as gripping delicate objects almost autonomously. Biological systems have similar properties and functions. In neither living nor non-living systems is the underlying materials science well understood. This program will explore analogies, and try to embed functions and properties into non-living systems that are similar to those in living systems. ii) Flames. Flames are prototypical dissipative systems: they also convert one form of energy (usually chemical free energy) into another form (heat). This project is not concerned with the use of this heat (as in an engine), but with the characteristics of flames as non-linear and complex systems. We are currently focused on the tendency for some model systems, when burning, to show behaviors expected of so-called “folded bifurcations:” that is, to show transitions between basins of attraction that are not reversible, but involve paths “forward” and “backward” between different stable states of combustion that are quite different.

FY 2014 HIGHLIGHTS

We continue to focus on the development of soft actuators and machines – machines whose structure involves soft and/or flexible organic materials (polymers, elastomers), and whose actuation is pneumatic or hydraulic. Recently completed projects in this area have broadened the movement capabilities and material properties of soft machines and will, in future work, facilitate the construction of actuators and tools that mimic some of the behaviors (and underlying mechanisms) of living systems. 1.1 Soft Actuators. In the area of actuation, we have developed strategies for (i) controlling large numbers (>50) of independent soft actuators, (ii) actuating pneumatic networks rapidly, and (iii) constructing soft actuators that are resistant to mechanical damage. 1.2 Composites of Elastomers and Other Materials. Our recent work in this area has focused on the development of composites and/or devices that are compatible with the anisotropic motion and range of movements required by soft machines. 1.3 Reconfigurable Systems. Soft machines that rely on pneumatic actuators are, in principle, easier to reconfigure than hard machines that rely on electronic components. We have developed several methods for using reversible couplings—magnetic and mechanical—to rapidly assemble (and re-assemble) soft machines.

Directed Assembly of Bio-Inspired Supramolecular Materials for Energy Transport and Capture: Mesoscale Construction of Functional Materials I

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Funding: \$759,000 (2014-2017)

PROGRAM SCOPE

The mesoscale engineering of nanoscale building blocks holds enormous promise to catalyze a revolution in new functional materials for advanced energy technologies. Bio-inspired systems can play a key role in this effort due to their inherent “programmable” function. In this program, we explore the use of controlled hydrodynamic flows for the directed assembly of synthetic peptides in microfluidic devices as a path to new functional materials. This strategy offers repeatable, mesoscale compositional and structural control of the assembled materials, with the potential for scalability. We capitalize on tailored microscale flow dynamics and peptide precursor reaction kinetics to bias assembly of peptide monomers into nanoscale and larger constructs. The hydrodynamic assembly method holds strong potential to enable fabrication of assemblies and hierarchical constructs that cannot form spontaneously in solution. In this way, directed assembly of synthetic peptides using microfluidics allows for unprecedented control of materials structure and properties at the nano and mesoscale. The overall goal of this research program is to understand the basic scientific foundation and the mesoscale materials design rules. In summary, the proposed work aims to “engineer” a new class of mesoscale functional materials. This new assembly strategy will fundamentally impact work in chemistry, physics, and materials science that will profoundly change how we think about designing and manipulating biomaterials.

FY 2014 HIGHLIGHTS

We are developing microfluidic device based approaches for fabrication of self-assembled polypeptide “nanostructures” with tailored materials properties. In this approach, flow fields in microfluidic systems are controlled in order to generate hydrodynamic flows that drive assembly of peptide materials. We are quantitatively characterizing the first microfluidic devices used to drive assembly at the flow interface between a flow focused, pH buffered monomer stream and an adjacent acid stream. This strategy facilitates geometric control of mesoscale structure. This initial year we are quantifying the device flow dynamics and the overall assembly kinetics. We have confirmed spectroscopically, and using Atomic Force Microscopy (AFM), the hydrodynamic control on polypeptide structure. We have acquired the first nanoscale images of these engineered materials. Moreover we are modeling the tailored microscale flow dynamics and reaction kinetics these 2-D linear flows, via COMSOL. This microfluidic-based method continues to show the potential and enables fabrication of assemblies and hierarchical constructs that cannot form spontaneously in solution. Given the wide array of macrostructures that can have synthesized using this strategy, we are developing new optical methods to image and study the electronic properties of the synthetic hydrogels formed in-situ. We have built a confocal spectral imaging system which allows us to probe how differences in hierarchical structure impacts the optical/electronic spectral properties and map the assembly kinetics as a function of peptide monomer structure. We are using molecular dynamics (MD) simulations to explore structural impact on assembly

dynamics and products. Techniques including nano CD, time-resolved non-linear microscopy, and x-ray analysis in the microfluidic reactors are being used.

DOE National Laboratories

Dynamics of Active Self-Assembled Materials

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Funding: \$976,000 (2014)

PROGRAM SCOPE

Dynamics of Active Self-Assembled Materials research program is focused on the fundamental aspects of out-of-equilibrium dynamics and self-assembly of bio-inspired materials for emerging energy applications. It paves the way for the discovery of tailored self-assembled materials and structures that can self-heal, regulate porosity, strength, water or air resistance, viscosity, or optical properties. The program synergistically combines experiment, theory, and simulations. It emphasizes strong cross-disciplinary ties with other research programs in Argonne, the Institute for Molecular Engineering of the University of Chicago, and leading soft matter groups in the USA and worldwide. This program makes active use of Argonne's scientific user facilities: the Center for Nanoscale Materials and Advance Photon Source. Our long-term goals are to develop fundamental understanding of out-of-equilibrium self-assembly in synthetic and bio-inspired systems as it relates to BES missions in Biomolecular Materials and Mesoscale Science. In the next three years we will explore new approaches to synthesis and discovery of a broad class of self-assembled bio-inspired materials stemming from the advances of our program: functional 2D and 3D self-assembled tunable and permanent structures built from functionalized sticky colloidal particles energized by applied electric or magnetic fields, and novel dynamic biomechanical materials formed by active swimmers (bacteria) placed in structured liquids (liquid crystals). For all these complex out-of-equilibrium systems we will develop predictive theoretical multi-scale description; the mathematical models will be implemented on GPU computers.

FY 2014 HIGHLIGHTS

Surfaces decorated with dense arrays of microscopic fibers exhibit unique materials properties, including superhydrophobicity and low friction. Nature relies on 'hairy' surfaces to protect blood capillaries from wear and infection (endothelial glycocalyx). Here we report on the discovery of self-assembled tunable networks of microscopic polymer fibers ranging from wavy colloidal 'fur' to highly interconnected networks. The networks emerge via dynamic self-assembly in an alternating electric field from a non-aqueous suspension of 'sticky' polymeric colloidal particles with a controlled degree of polymerization. The resulting architectures are tuned by the frequency and amplitude of the electric field and surface properties of the particles. We demonstrate, using atomic layer deposition, that the networks can serve as a template for a transparent conductor. These self-assembled tunable materials are promising candidates for large surface area electrodes in batteries and organic photovoltaic cells, as well as for microfluidic sensors and filters. Source: Demortiere *et al*, Nature Communications, v 5, p 3117 (2014).

Active Assembly of Dynamic and Adaptable Materials

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Funding: \$1,251,000 (2014)

PROGRAM SCOPE

The fundamental goal of this project is to understand and apply key principles used by living systems to develop materials whose transport, reconfiguration, and disassembly can be programmed or “self-directed” in controlled environments. Our long-term goal is to learn how to develop robust, energy-dissipative “nano-robots” that replicate many of the emergent behaviors of living systems (e.g., the ability to adaptively change color) within artificial nanocomposites. The scope of this program includes two primary themes: (i.) Active Protein Assemblies that involves the *ex vivo* use of kinesin and tubulin to assemble, manipulate, and dynamically organize hybrid and composite nanomaterials; and (ii.) Artificial Microtubules that is focused on the design and development of robust artificial analogues to the energy-consuming protein tubulin. Work on Active Protein Assemblies has focused on applying the work produced by kinesin and microtubules to actively assemble non-equilibrium structures such as ring nanocomposite, lipid nanotube networks, and heterostructured nanowires. Work on Artificial Microtubule has centered on using computational and synthetic approaches to develop peptide- and polymer-based “building blocks” capable of mimicking the structure and dynamic self-assembly of natural microtubules.

FY 2014 HIGHLIGHTS

Electrostatics and Microtubules – Understanding of how the electrostatic state of the C-terminal tubulin tails regulates the mechanical properties (i.e., persistence length) and polymer dynamics (i.e., dynamic instability) of microtubule filaments, as well as their interaction with kinesin motors. Directed Self-Assembly (DSA) – Combined experimental and theory (molecular dynamics simulation) approaches to describe the DSA of microtubule filaments into one-dimensional nano-arrays. CdS Nanotubes – Described a synthetic, biomimetic strategy to control the uniform growth of cubic zinc-blended cadmium sulfide (CdS) nanocrystals on microtubule (MT) templates, replicating the microtubule’s tubular morphology with dense CdS only a single nanocrystal thick. Microfluidic Protection – Developed novel PDMS microfluidic device to microfluidically deoxygenate reaction solutions, and regulate the formation of photo-oxidative byproducts that adversely affect kinesin motor transport and assembly of nanocomposite structures. Peptide Assemblies – Combined experiments and self-consistent field theory to study the role of amphiphilic character, hydrogen bonding behavior, and distribution of charges in the supramolecular self-assembly of asymmetrically functional, wedge-shaped peptides. Chirality in Tubules – Using molecular dynamics simulation, the essential, underlying interactions that regulate the self-assembly of tubular nanostructures with specific chirality were described. Thermally-regulated Assembly/Disassembly – Developed an efficient and practical synthetic protocol for N-alkyl bis-

maleimide crosslinkers using a reverse Diels–Alder reaction, enabling an approach for temperature-regulated assembly and disassembly of polymer filaments

Molecular Nanocomposites

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Funding: \$1,416,000 (2014)

PROGRAM SCOPE

The goal of the Molecular Nanocomposites project is to explore the assembly and unique emergent properties of bioinspired, nanocomposite materials created using solution-based processing methods. We seek to develop fundamental understanding and control of molecular assembly mechanisms on multiple length scales, the physical and chemical properties derived from such nanoscale assemblies, and the implications of these properties for DOE's energy mission. The Molecular Nanocomposites project is comprised of two tasks: Adaptive and Reconfigurable Nanocomposites (Task 1, PI Dale Huber) and Complex Nanocomposites (Task 2, PI Jeff Brinker). The goal of task 1, Adaptive and Reconfigurable Nanocomposites, is to explore the basic science associated with the use of energy consuming, switchable, and/or responsive components to create programmable and/or reconfigurable nanocomposites. The task aims to understand how responsive nanoparticles, surface functionalization, and organic overlayers can be used in concert to influence physical properties of both primary particles and assembled composites. The goal of Task 2, Complex Nanocomposites, is discovery and understanding of new chemically- and physically-based synthesis and assembly methodologies to construct and integrate complex porous and composite materials which exhibit structure and function on multiple length scales. It aims to establish processing-structure-property relationships for new nanocomposites prepared by self-assembly, directed assembly and templating procedures pioneered by the team members. Emphasis is on construction of 3D nanocomposites with dimensional scales and interfacial behaviors designed to allow energy conversion, transduction, or storage and/or enable biotic/abiotic integration and development of life-like structure and functionality.

FY 2014 HIGHLIGHTS

In the past fiscal year, a broad range of new approaches were developed to predict, program, control and observe the directed assembly of complex nanocomposites. FY 2014 highlights included several first demonstrations, including (a) use of switchable PNIPAM surfactants on nanoparticle arrays to reversibly actuate interparticle energy transfer, published by Dale Huber and Hongyou Fan in ACS Nano in 2014,

(b) development of pressure-directed assembly as non-chemical method for systematic tuning of interparticle distance for investigation of energy transfer and optical properties under stress, published by Hongyou Fan in Nature Communications in 2014, (c) development and characterization of surface functionalization for tethered and cushioned supported lipid bilayers to enable flexible control of lipid bilayer properties, published by Darryl Sasaki in Langmuir in 2014 and (d) development of curvature sensing molecular assemblies for the selective partitioning and attachment of proteins to structured lipid membranes, published by Darryl Sasaki, Dale Huber, and Carl Hayden in JACS in 2013. In addition, a new software release of the Tramonto-5.0 fluid density functional theory (F-DFT) code was delivered in October 2013. These theories compute fluid structure near surfaces or as a result of self-assembly, and v 5.0 includes updates to capabilities in grafting polymers to surfaces: https://software.sandia.gov//tramonto/release_notes.html. Overall, 12 publications were supported by this project, including papers in ACS Nano (2), Nature Communications, JACS, Accounts of Chemical Research, Nanoscale, Langmuir, and J. Phys. Chem. Letters. Work under this project received a spring 2014 Spring MRS Best Poster Award and 2013 Federal Laboratory Consortium "Notable Technology Development Award" for 'Self-Assembled Multifunctional Optical Coatings'.

Clathrin Biotemplating

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Funding: \$335,000 (2014)

PROGRAM SCOPE

The focus of this multi-disciplinary research program is to characterize and exploit the tailored molecular interactions inherent in biological systems. Such understanding will enable deterministic formation of complex organic/inorganic constructs and engineering of responsive, biomimetic materials that exhibit self-healing and self-regulating transformations. These materials will lead to fundamentally new designs in biomimetic organic/inorganic devices for energy storage, catalysis, solar cells, and fuel cells. The team integrates a wide range of experimental and theoretical approaches to assemble, characterize, and model dynamic assembly. Our recent collaborative effort has focused on experimental and theoretical insights into the fundamentals of biomimetic self-assembly in two and three dimensions, investigating the effects of multivalency on hierarchical assembly processes, extending our strategy for non-covalent, site-specific functionalization of clathrin protein assemblies to template multiple inorganic species simultaneously on the same protein particle, and developing advanced x-ray characterization techniques for atomic scale resolution of biomaterials with local order but disorder at large length scales.

FY 2014 HIGHLIGHTS

(1) Correlated X-ray Scattering (CXS) of soft materials: Tools to study disordered systems with local structural order, such as proteins in solution, remain limited. The Doniach lab has recently achieved a breakthrough in X-ray science by demonstrating for the first time the feasibility of CXS to obtain structural information at atomic resolution for disordered systems of ordered objects. In our

publication, we report on experimental work in which CXS signals were obtained for an ensemble of 20 nm silver nanoparticles in three dimensions. (2) Theoretical modeling of clathrin structure and responsive transformations: We developed a theoretical model of a clathrin protein lattice on a flexible membrane. Through Monte Carlo simulations, we predict the equilibrium phase behavior of clathrin lattices at various levels of tension, predicting the conditions where the lattice exhibits solid and fluid phases. We address the impact of membrane fluctuations and nanoscale indentations in modulating the local phase behavior of the clathrin lattices. Our work provides a basis for utilizing local deformations in triggering 3-dimensional vesicle budding from reorganization of 2-dimensional clathrin lattices. (3) A biomimetic system for 2-dimensional assembly of multi-functional subunits: In order to extend the lessons learned about the self-assembly of clathrin, we have designed new systems that can be produced in larger quantities and tailored to our specific needs. We are employing lithography based nanofabrication techniques to create self-assembling particles across the 100 nm – 10 μm scale with several of the characteristics of clathrin (3-legged structure, localized binding sites, propensity to attach to 2D interfaces) in order to analyze their self-assembly dynamics. By selective functionalization of the particle faces, we can order them onto fluid 2D air-water interfaces and manipulate their self-assembly structurally and chemically.

Bioinspired Materials

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David Vaknin; Ames Laboratory
Students: 3 Postdoctoral Fellow(s), 4 Graduate(s), 0 Undergraduate(s)
Funding: \$643,000 (2014)

PROGRAM SCOPE

Nature is replete with hierarchically assembled hybrid materials where the multi-scale structures confer unique properties and functions. The objective of the Bioinspired Materials FWP is to explore biomimetic pathways for design and synthesis of hierarchically self-assembled functional materials with controllable properties for energy applications. Our approach mimics Nature using organic templates coupled to mineralization proteins to control the growth of the inorganic phase to form self-assembled nanocomposites. Magnetotactic bacteria with chains of magnetic nanocrystals serve as inspiration and sources of mineralization proteins. We are developing new methods to create dynamic tunable nanostructures using reversible linkages for assembly/disassembly of inorganic nanocrystals in response to environmental conditions. This highly interdisciplinary research is facilitated by FWP investigators with diverse backgrounds in several disciplines. The synergistic combination of synthesis, materials characterization and theory provides a powerful approach for understanding mineralization processes in Nature and for expanding on these processes to grow novel nanocrystals in organic matrices *in vitro*. This controlled bottom-up approach for materials design aligns well with DOE's proposed directions in "control science", allowing for the synthesis of nanostructures such as complex magnetic nanocrystals with potential energy relevance.

FY 2014 HIGHLIGHTS

We synthesized novel magnetic nanomaterials using magnetotactic bacteria as inspiration and as a source of the biomineralization protein Mms6. While the controlled, low-temperature fabrication of uniform superparamagnetic nanocrystals remains a challenge, bioinspired routes offer room-temperature pathways for the production of many complex magnetic nanocrystals with desirable shapes and sizes. We continue to develop experimental methods, guided by theory and computation, to control the placement and self-assembly of the nanocrystals into bioinspired mesoscale structures. To expand our knowledge of biomineralization proteins beyond Mms6, we have investigated proteins from different strains of magnetotactic bacteria and developed predictive models for assembly of such nanocrystals using DNA and polymer-based strategies. Operationally, we have developed methods to pattern surfaces with arrays of magnetic nanocrystals by selectively localizing the mineralization proteins on surfaces as well as developed scattering and spectroscopy methods to investigate the biomineralization process and the interaction of the biomineralization proteins with various monolayer surfaces and with iron.

Molecularly Engineered Biomimetic Nanoassemblies

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Sr. Investigator(s): Andrew Shreve; New Mexico, University of
Hsing-Lin Wang; Los Alamos National Laboratory
Reginaldo Rocha; Los Alamos National Laboratory
Sunil Sinha; California-San Diego, University of
Students: 1 Postdoctoral Fellow(s), 3 Graduate(s), 0 Undergraduate(s)
Funding: \$365,000 (2014)

PROGRAM SCOPE

We are rapidly approaching the next revolution in materials science where first principles design will yield the assembly of materials having specific emergent properties. An especially rich area for this transformation to be realized is in the assembly of materials that absorb, transport, or manipulate light energy. Natural light-harvesting systems provide exquisite examples of such materials through genetically encoded assemblies that are dynamic, repairable, and tunable in response to external stimuli. We can predictively create materials with similar functionalities if only we can develop: bright chromophores with broad spectral coverage, photostability, and high fluorescence quantum yields; predictive models for assembly of these chromophores to control light absorption, emission and energy transfer over defined distances; and control over the dynamics of assembly. Toward reducing those gaps in knowledge, we will mimic Nature and develop optically and electronically active molecular components with unique size and intermolecular optical phenomena, and then assemble these materials into complex architectures by taking advantage of recent advances in predictive *de novo* protein design and DNA assembly. This materials fabrication approach allows us to fine-tune the emergent optical and electronic properties. Interwoven through the entire project is a characterization effort that addresses both functional and structural characterization of the resultant materials. The targeted assembly types and methods also allow study of materials ranging from classic 2D self-assembled thin films systems to multi-layer and bulk materials. Overall, we anticipate gaining

fundamental knowledge of how to manipulate light energy using new types of chromophores and their assemblies, a consistent thrust throughout our program past and future.

FY 2014 HIGHLIGHTS

We aim to generate materials with characteristics inspired by the complex assemblies found in Nature, producing chromophores and their functional assemblies with both tunable and adaptive behavior, and producing materials capable of control of light harvesting. Toward mimicking Nature, we 1) develop new chromophores (fluorescent noble-metal nanoclusters and conjugated organic oligomers); 2) develop DNA and computationally designed peptide assemblies; and 3) apply a suite of characterization tools to understand their emergent properties upon assembly. 1) We have created a pH sensitive fluorescent and white light emissive chromophore of polyphenylene vinylene oligomer (OPP) that shows controlled intermolecular charge transfer; a fluorescent tyrosine-OPP; and redesigned a 2D conjugated thiophene polymer. 2) We have used Rosetta Design to create helical peptides that assemble into planar mesoscopic hexagonal arrays and have imparted those assemblies with temperature-dependent changes in hexagon size, through addition of a genetically engineering elastin polymer. 3) We have templated an Au₁₄₄ cluster within elastin peptides [Au₁₄₄ clusters are directly between the size of clusters (10s of metal atoms) and particles (100s of metal atoms, plasmonic)]. Additionally, we have utilized a previously created and highly stable fluorescent nanocluster (DNA templated) to study its photophysical behavior upon assembly through DNA base pairing or controlled aggregation. We find that the cluster undergoes a series of reversible energy transfer reactions between the monomer to dimer to trimer nanocluster, until finally the monomer is fully consumed and the remaining fluorescence is from the near-IR emitting trimer nanocluster (a first in the cluster community). Further, we have created a cationic OPP that takes on new emergent properties upon incorporation within genetically engineered elastin assemblies.

Directed Organization of Functional Materials at Inorganic-Macromolecular Interfaces

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Anthony van Buuren; Lawrence Livermore National Laboratory
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Funding: \$631,000 (2014)

PROGRAM SCOPE

We are investigating controls on directed organization in biomimetic systems, and the links between organization and function that emerges from assembly of nanoscale components. In one study, we utilize phospholipid bilayers on Si nanowires as a basic bionanoelectronic device scaffold. The bilayer produces a barrier against ion transport and provides an artificial environment for membrane proteins. We are performing studies of protein and lipid assembly process, characterizing the atomic scale structure using x-ray scattering, and assessing energetic parameters controlling organization via kMC models. We are incorporating these structures in working multi-component bioelectronic devices and show how complex device functionality emerges from a combination of materials properties and targeted protein functionality. We have also been designing and building novel biomimetic components that could take over the role of membrane proteins in these structures. In a second set of studies, we are investigating the dynamics of macromolecular self-assembly into 1D and 2D ordered structures in

systems where required conformational changes limit assembly kinetics. We exploit variations in solvent composition and substrate chemistry to manipulate interactions and control the resulting architecture. We use *in situ* AFM and TEM investigate assembly dynamics, micro-Raman/FTIR and force spectroscopy to identify and quantify intermolecular interactions, and MD and kMC simulations to test mechanistic models of assembly. We are also utilizing DNA origami as a scaffold upon which to build heterostructures with Au nanoparticles and MS₂ viruses. The latter are modified to include light adsorbing centers for light harvesting. Light harvesting efficiency is measured as a function of virus-virus and virus-nanoparticle spacing and the results are compared to predictions based on finite-difference time-domain numerical simulations.

FY 2014 HIGHLIGHTS

(1) Demonstrated multicomponent assembly of bioelectronic devices involving ionophores and light-activated membrane proton pumps that perform biological regulation of device activity. (Advanced Materials, 2014). (2) Refined synthetic conditions for producing CNT porins- biomimetic analogs of ion channels. Characterized structure and transport properties of the CNT porins using cryo-TEM, single molecule transport studies, and bulk transport studies. (Nature, 2014; Nano Letters, 2014). (3) Used high-speed AFM for in-situ monitoring of dynamin protein assembly on lipid-coated nanowire templates. Obtained the first images of GTP-induced disassembly of the protein complex from a curved template. (Manuscript in preparation, 2014). (4) Used a combination of SAXS and STXM to determine atomic level structural ordering in lipid bilayers adsorbed on the SiNW surface. (submitted, Advanced Materials Interfaces). (5) Used SAXS to study the formation and bilayer structure of (DOPC) coating on Silicon nanowires (SiNWs) as a host matrix for self-directed reconstitution of Proteorhodopsin (pR) protein membrane. (6) Exploiting the ability of vicinal sapphire surfaces to induce block alignment in block copolymer films, we showed that S-layer protein assembly on such films is directed exclusively along the blocks. (7) Used *in situ* TEM and AFM to investigate both Ca-induced globule formation by polyelectrolyte polymers chosen to mimic protein scaffolds in biominerals and the subsequent mineralization of the globules (in revision Nature Materials). (8) Developed a new bioconjugation strategy that utilizes potassium ferricyanide-mediated oxidative coupling to attach aniline-functionalized AuNPs to o-aminophenol-containing oligonucleotides, peptides, and proteins. (Bioconjugate Chem, 2014). (9) MD simulations of a bead-spring model of collagen showed that all of the architectures observed experimentally could be reproduced with a periodic arrangement of strong and weak bead-bead interactions (Langmuir, 2014).

Soft Matter Physics

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Funding: \$699,000 (2014)

PROGRAM SCOPE

The primary goal of the group is to understand the effects of mesoscopic confinement and the role of self-assembly in soft materials through the use of nano-patterned templates and well-defined interfaces. We use synchrotron x-ray scattering and scanning probe techniques to study fundamental

properties of biomolecular materials, simple liquids, complex fluids, molecular and macromolecular assemblies, and polymers at liquid-vapor, liquid-solid and liquid-liquid interfaces. The challenges are (1) to understand interfacial and nanoscale confinement effects of liquids including the relationship between macroscopic phenomena and nanoscale behavior, (2) how templates, confinement and molecular anisotropy can be used to direct the assembly properties of soft matter including molecular orientations and long-range positional order, (3) to understand how similar self-assembly behavior arises for a wide variety of systems (4) how order correlates with function. Structural aspects of self-assembly in thin organic films underlie many emerging organic based devices and energy technologies. The Group has carried out measurements at NSLS (BNL) and APS (Argonne) and has an approved Partner User Proposal at the Soft Matter Interfaces Beamline at NSLS II.

FY 2014 HIGHLIGHTS

Superhydrophobicity, a bioinspired phenomenon, was investigated using x-ray diffraction in arrays of ~20 nm-wide silicon textures with cylindrical, conical, and linear features. The superhydrophobic state was found to vanish above critical pressures that depend on texture, shape, and size, in agreement with classical capillary theory. Fabricated superhydrophobic surfaces with well-defined geometries at the 10-nm scale using diblock-copolymer assisted lithography. The anti-icing properties of the surfaces have been characterizing using high-speed optical imagery, water droplet freezing, and ice adhesion experiments. The nanopatterned surfaces delayed ice formation and dramatically reduced ice adhesion. The analysis of the X-ray Reflectivity from a series of alkane-water interface show that the width of the potential hydrophobic gap at these oil-water interfaces is significantly smaller than the values previously reported. Demonstrated via *in situ* SAXS measurements the assembly of a body-centered cubic lattice of P22 virus-like particles (VLP) electrostatically induced by mixing peptide linker-tethered P22 VLPs with smaller and oppositely charged dendrimers in solution. X-ray reflectivity structural measurements of the of silicon oxide in contact with bulk liquid or vapor octadecanol. Over a range of temperature (~ 12 °C) above the freezing point of C¹⁸OH an extremely well defined monolayer forms at the solid interface that consists of well-packed, surface-normal molecules. X-ray reflectivity measurements of silicon substrates reveal for the first time the existence of a thin, low density layer intruding between the single-crystalline silicon and the amorphous native SiO₂ terminating it. The inclusion of this layer is essential for an accurate determination of the structure of soft materials on these interfaces. Octadecyltrichlorosilane self-assembled monolayers on sapphire (0001) show the existence of a pseudo-rotational epitaxial monolayer.

EARLY CAREER: Real-Time Studies of Nucleation, Growth and Development of Ferromagnetism in Individual Protein-Templated Magnetic Nanocrystal

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Funding: \$500,000 (2014)

PROGRAM SCOPE

The research of the Emergent Magnetic and Atomic Structures Group is aimed at determining the nature of macromolecule-mediated magnetic nanoparticle formation: i.e., the mechanism of particle

nucleation, growth, the emergence of crystal structure and development of ferromagnetism in the individual bio-templated magnetic nanocrystal by utilizing the advanced electron microscopy techniques. Uniform magnetic nanoparticles with large magnetic moment and controlled magnetic anisotropy have important technological applications from data storage, to catalysis and drug delivery. Biomimetic synthetic routes offer room-temperature pathways to placement control, formation, and assembly of a variety of magnetic nanostructures with unique shapes and sizes. We work on gaining a better understanding on how the assembly of biomacromolecules dictates nanoparticle formation and functional properties. Magnetite biomineralization by magnetotactic bacteria is used as model system with the individual microorganisms monitored throughout the various steps of the biomineralization process.

FY 2014 HIGHLIGHTS

Iron biomineralization can be induced and tuned to yield a variety of biogenic magnetic materials. Iron can be biomineralized by many different microorganisms, and tweaking this process exerts control over the magnetic properties of biogenic materials. Biomioneralization can be induced and/or tweaked to yield nanocrystals with tunable composition and magnetic properties. Moreover, comprehensive characterization of biominerals has revealed the key factors affecting bacterial iron biomineralization.

Electron and Scanning Probe Microscopies

Institutions Receiving Grants

Discovery of Dielectric Response and Forces in Sub-Nanoscale Objects

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Funding: \$360,001 (2014-2015)

PROGRAM SCOPE

This project explores dielectric response in nano-structured materials, using inelastic and elastic scattering of an Angstrom-sized kilo-volt electron beam. This information will be useful for better understanding of light-matter interaction in wide ranging fields such as photo-catalysis, energy harvesting of sunlight, and information transmission in semiconductor structures using optical waveguides. Electron beams are particularly useful for this exploration, because they are capable of applying very wide bandwidth driving fields into very small volumes, revealing electronic behavior that could be put to practical use in an appropriately engineered structure. As we extend the energy scale of these studies into energy extremes, ranging from vibrational and plasmonic modes in the 10-300 meV range on the low end, and out to core losses and multiple single particle excitations in the KeV energies, we are seeking to interpret energy loss spectral information in terms of a time domain summary of specimen behavior from attosecond to picosecond time scales.

FY 2014 HIGHLIGHTS

During the present award period, we have largely completed our understanding of repulsive lateral forces on nanoparticles created during the close passage of a KeV electron. The results are surprising, and so we have been making extensive checks during this year to verify and begin exploration of implications. First, we have found that repulsive forces in nanoparticles are multipolar in character and occur during atto-second time of the very close approach of the swift electron. A key feature of our understanding is that magnetic interactions with nano-particle surface currents are necessary to understand the behavior. We find also very large forces in short wavelength patterns on the surface and within the nano-particle. Finally, in Au, we also notice evidence for collective behavior of 4d electrons, resulting in a high energy plasmonic mode near 25 eV. Dipole, optical energy plasmonic interactions do contribute to lateral forces, but at levels much smaller than the close-in multipolar modes. A manuscript is completed and being readied for submission. With the arrival of the Nion Ultra-STEM with the Hermes monochromator, we have spent extensive effort in initial instrumental operation, learning, and environmental work. We have demonstrated a 9 meV energy resolution -- a world record result -- and have begun studies of vibrational and interband excitations in various materials in collaboration with other workers. Results have appeared in Nature Letters, 514 209-212 (2014). The theoretical understanding accomplished here, together with the instrumental work to push the energy resolution and acquisition accuracy in the new instrument, provides a strong footing to accomplish the goal of

deriving time domain information from EELS spectra as promised in the Program Scope. This activity has also resulted in three invited presentations at international meetings.

EARLY CAREER: Mapping Interactions in Hybrid Systems with Active Scanning Probes

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Sr. Investigator(s):
Students: 0 Postdoctoral Fellow(s), 2 Graduate(s), 3 Undergraduate(s)
Funding: \$150,000 (2014)

PROGRAM SCOPE

The goal of this research is to explore nanoscale interactions in hybrid systems by harnessing the precision and flexibility of scanning probe microscopy. Projected applications in areas such as energy conversion, opto-electronics, and spintronics will involve hybrid nanosystems composed of two or more materials or nanostructures which interact electrically, optically, or magnetically. Progress in understanding these interactions has been held back by cumbersome and/or imprecise fabrication methods. To overcome this challenge, this work will employ cantilevers with integrated active magnetic and optical components. These active probes will be controllably scanned in proximity to metal or semiconductor nanoscale structures, essentially creating a highly tunable and versatile hybrid system. This technique will allow detailed studies of interactions between optical resonators and plasmonic or spintronic nanostructures, or between dynamic ferromagnetic elements and quantum-confined electron spins. Scanned probes with an integrated optical resonator will be used to spatially map the coupling of the resonator's evanescent modes to nanoscale emitters, such as semiconductor quantum dots. Probes with radio-frequency-driven ferromagnetic microstructures will allow us to study the effect of a highly localized, dynamic magnetic field on confined electron spins. The planned research offers a significant increase of flexibility and efficiency for investigating hybrid systems over traditional nanoassembly, accelerating progress towards future technology.

FY 2014 HIGHLIGHTS

As we move towards the objective of coupling nanostructures to optical and magnetic devices fabricated on scanned cantilevers, we have obtained results on the individual components separately, before they are ultimately combined. We have constructed a combined confocal optical/scanned probe microscope, and have used optical microscopy capabilities to study photoluminescence dynamics of individual nanocrystal quantum dots. We have measured the absorption spectrum of single quantum dots at room temperature, and extracted information about broadening mechanisms [1]. We have also studied magnetization dynamics of driven ferromagnetic microstructures using a sensitive double-modulation technique. These results provide a detailed look at how magnetic domains dynamics are affected by disorder [2]. We have currently begun combining the optical and scanning probe microscopy capabilities of our setup, measuring the effect of a local electric field on quantum dot emission dynamics. [1] 'Homogeneous and inhomogeneous sources of optical transition broadening in room temperature CdSe/ZnS nanocrystal quantum dots' M. Wolf and J. Berezovsky, Applied Physics Letters 105, 143105 (2014). [2] "Magneto-Optical Imaging of Vortex Domain Deformation in Pinning Sites" R. Badea, J. A. Frey, and J. Berezovsky, arXiv:1410.4518 [cond-mat.mes-hall] (submitted to Journal of Magnetism and Magnetic Materials).

Application of STEM/EELS to Plasmon-Related Effects in Optical Spectroscopy

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Funding: \$150,000 (2014)

PROGRAM SCOPE

We are currently studying the (1) plasmonic energy transfer from metallic nanoparticles to neighboring materials and (2) Localized surface plasmon resonance (LSPR) and plasmon coupling in alloy nanoparticles. Understanding plasmonic energy transfer is important for developing superior photocatalytic and photovoltaic devices. Using our monochromated STEM/EELS, we are able to probe the energy transfer process at the single-particle level with high energy resolution (~120meV). The second program is based on alloy nanoparticles synthesized via pulsed laser induced liquid thin film dewetting. With this method, we can control the mole fractions of the metal and perform comprehensive studies on the tuning effects of the alloy compositions on LSPRs. Also, we are able to design and pattern nanoparticle arrays to study the collective properties of the LSPRs.

FY 2014 HIGHLIGHTS

In the first year of this proposal we have concentrated on the observation of Fano interferences using optical and electron energy-loss spectroscopies (EELS). Our experimental observations were fully correlated with continuum electrodynamics simulations and demonstrate that the mechanism responsible for optically-driven Fano resonances is similar to the EELS counterpart. As a follow-up to our work on the observation of Fano interferences in silver nanocubes, we are currently investigating the effects of substrates with varying refractive indices on the hybridization and damping of the LSPRs in silver nanocubes with 3D STEM/EELS tomography.

Nanoscale Properties of Novel Materials

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

The conducting interface that forms between the two band insulators LaAlO₃ (LAO) and SrTiO₃ (STO) has attracted a lot of interest since its discovery almost a decade ago. In the past few years, this system has proved to be a trove of interesting new physics, showing a gate-tunable conductance, superconductivity, and magnetism, among other effects. Particularly intriguing is the superconductivity and ferromagnetism, normally antagonistic phenomena, which we discovered can coexist at the interface in

appropriately grown samples. The major part of this project is devoted to investigating the nature of both the magnetism and the superconductivity at the LAO/STO interface, using electrical transport and eventually low temperature scanning probe techniques. The epitaxial films used in these studies were synthesized in the group of Prof. Chang-Beom Eom at the University of Wisconsin, Madison. The transport experiments focused on measuring the resistance of gated LAO/STO interface structures as a function of magnetic field at temperatures ranging from 25 millikelvin to room temperature in order to study the interplay between superconductivity and magnetism. These experiments involved both large two-dimensional films, as well as smaller, sub-micron structures defined by electron-beam lithography. The scanning probe work has been devoted to the development of a millikelvin range scanning probe microscope capable of performing atomic force microscopy, electrostatic force microscopy and magnetic force microscopy. Once operational, this microscope will enable us to correlate the magnetic and electronic properties of LAO/STO interface devices on the scale of a few hundred nanometers.

FY 2014 HIGHLIGHTS

The LAO/STO interface system offers a unique platform to study the superconductor-to-insulator transition (SIT), as the interface can be tuned from the superconducting state to the insulating state by means of an electric field applied by putting a voltage on a back or top gate. As with other disordered superconducting systems, it can also be tuned out of the superconducting state by applying a magnetic field, the so-called field-tuned SIT. Recently, we studied the field-tuned SIT in back-gated LAO/STO interface structures, and found a critical exponent product $z\nu \sim 7/3$, indicating that the transition is governed by quantum percolation effects. While such critical exponents have been reported previously for high resistance films, they have not been reported for a low resistance system like ours, with a maximum sheet resistance of ≈ 1.5 kohms much less than the quantum of resistance $R_Q \sim h/4e^2 = 6.45$ kohms. [Phys. Rev. B 90, 100506(R) (2014).] Scanning probe microscopes that use quartz crystal tuning forks as force transducers require instruments that can measure frequency shifts with a resolution of a few millihertz. Typically, this is done with a phase-locked loop (PLL), but to obtain the required frequency resolution, a digital signal processor (DSP) is required, greatly increasing the complexity of the instrument. We have designed and developed a hybrid analog-digital PLL that combines the simplicity of an analog front-end with the frequency resolution of a direct digital synthesis (DDS) chip that is controlled by a simple microprocessor. This has been successfully used in our home-built scanning probe microscope. [Rev. Sci. Instrum. 85, 013707 (2014).]

Structure and Dynamics of Domains in Ferroelectric Nanostructures

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Funding:	\$160,000 (2014)

PROGRAM SCOPE

The program is centered on investigating the formation of mesoscale domain structures and their evolution in ferroelectric thin films and nanostructures under an electric and/or mechanical stress field. The main objective is to understand the fundamental thermodynamic stability of ferroelectric domain walls and multi-domain configurations as well as dynamic mechanisms of domain switching using the

phase-field method. The focus will be on BiFeO₃ and PbZr_xTi_{1-x}O₃ (PZT) systems. BiFeO₃ is one of the most promising single-phase candidates for magnetoelectric device applications and one of the most scientifically fascinating materials that may exhibit electric polarization, oxygen octahedral rotation, antiferromagnetic order, strain, and significant ionic/electronic charges while PZT is currently the most widely utilized class of ferroelectrics for piezoelectric device applications. The research is being carried out in close collaboration between the PI's group and a number of world-class experimental groups who use High Resolution Transmission Electron Microscopy (HRTEM), *in situ* TEM with Scanning Probe Microscopy (SPM), or Piezoresponse Force Microscopy (PFM) to characterize the domain structures and dynamics in high-quality ferroelectric BiFeO₃ and PZT thin films.

FY 2014 HIGHLIGHTS

(1) Fundamental Understanding of BiFeO₃ Domain Wall Energies and Structures: We determined the atomic structures and energies of domain walls in BiFeO₃, combining DFT+U calculations and aberration-corrected TEM images. The calculated wall energies (γ) follow the sequence $\gamma_{109^\circ} < \gamma_{180^\circ} < \gamma_{71^\circ}$ for the 109°, 180°, and 71° walls. We attribute the high 71° wall energy to an opposite tilting rotation of the oxygen octahedra and the low 109° wall energy to the opposite twisting rotation of the oxygen octahedra across the domain walls. We quantitatively analyze the domain walls (DWs) in BiFeO₃ and successfully explain the unusual ferroelectric DW width and energy in BiFeO₃. (2) Understanding Ferroelastic Domain Switching Dynamics under External Excitations: We analyzed the microscopic behavior of individual ferroelastic domains under electric fields and mechanical stress in a thin PbZr_{0.2}Ti_{0.8}O₃ film using *in situ* transmission electron microscopy and phase field modeling. We found that the mobility and switching behavior significantly depends on specific microstructures. Our results provide new insights into understanding of polarization switching dynamics and suggest a route to engineer electromechanical devices. (3) Discovered a First Order Morphological Transition of Ferroelastic Domains in Ferroelectric Thin Films: Ferroelastic domains in epitaxial films are often pinned by interfacial dislocations. The morphology of a pinned ferroelastic domain in Pb(Zr_{0.2}Ti_{0.8})O₃ (PZT) thin films is investigated as a function of film thickness using phase field modeling in combination with transmission electron microscope (TEM) observations. It is found that the ferroelastic domain undergoes a first-order morphological transition from a domain fully extended through the film thickness to one terminated inside the film as film thickness increases. It is demonstrated that this transition is first-order associated with abrupt changes in thermodynamic properties of the domain structure at the transition.

Combined Microscopy Studies of Complex Electronic Materials

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Funding: \$180,000 (2014)

PROGRAM SCOPE

Many interesting electronic materials have very complex microstructure and exhibit high sensitivity to experimental conditions such as strain. Studies of small homogeneous single crystals under carefully controlled conditions are therefore needed for determining their fundamental properties. The goal of this program is to understand key aspects of important materials by combining multiple microscopy,

scanning probe and transport techniques with simultaneous control of temperature, strain, magnetic field, and vapor environment. We focus on VO₂ as a prototypical strongly correlated material, and monolayer dichalcogenide semiconductors of formula MX₂ as examples of a rich new class of electronic materials that are only available as small crystals and are susceptible to substrate, strain and environmental influence.

FY 2014 HIGHLIGHTS

A strain-controlled microscopy technique was developed with the initial aim of establishing the phase diagram of vanadium dioxide in the vicinity of the metal-insulator transition. It allowed us to determine the equilibrium boundaries between the three solid phases with unprecedented control and precision as a function of temperature and axial stress, and to locate the triple point, which coincides with the transition temperature at 65.0°C, to within a measurement accuracy of 0.1°C. In collaborative work, analysis of the scanning photocurrent microscopy of suspended single-crystal nanobeams showed that the photoresponse of vanadium dioxide is photothermal. Transmission infrared micro-spectroscopy on vanadium dioxide plates yielded the anisotropic phonon parameters and low frequency optical conductivity. Ultrafast pump-probe reflection measurements revealed that the electronic response time scale varies from just 40 fs to 200 fs between individual crystals. We also grew high quality monolayers of molybdenum disulfide and tungsten diselenide, as well as in-plane lateral monolayer heterojunctions. We created the first light-emitting diodes from lateral p-n junctions in monolayer tungsten diselenide. Bright electroluminescence was obtained with 1000 times smaller injection current and 10 times smaller linewidth than in earlier structures. By increasing the injection bias we could tune the electroluminescence between regimes of impurity-bound, charged, and neutral excitons. Using polarization-resolved photoluminescence we showed that in bilayers the emitted polarization can be continuously tuned through zero as a function of gate voltage, constituting the first demonstration of electric field control of orbital magnetic moments. We also observed linear splitting of the circularly polarized photoluminescence peaks in perpendicular fields up to 7 T, as well as magnetic tuning of the polarization, representing the first successful magnetic manipulation of valley pseudospin.

Development and Application of *In Situ* Nanocharacterization to Photocatalytic Materials for Solar Fuel Generation

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Funding: \$170,000 (2014)

PROGRAM SCOPE

We are developing a fundamental understanding of heterostructured semiconductor-based photocatalysts for H₂ generation via water splitting. Our catalysts are composite materials consisting of light harvesting semiconducting oxides supporting catalytic nanoparticles that facilitate the transfer of excited electrons/holes for water reduction/oxidation. We are working on titania and tantalate light harvesting oxides which are functionalized with metal and metal oxide nanoparticles yielding model systems which are active under ultraviolet light. The H₂ evolution is measured in a photoreactor and advanced electron microscopy techniques (including *in situ* and *operando* approaches) are employed to

elucidate structure-reactivity relations. We are also developing and employing high energy resolution electron energy-loss spectroscopy to obtain new insights from high spatial resolution vibrational spectroscopy and band gap determinations.

FY 2014 HIGHLIGHTS

There have been three major accomplishments within the current fiscal year: (1) Instrumentation – We have completed the design and construction of a gas handling system for our newly installed aberration corrected environmental transmission electron microscope. This is required to carry out *in situ* studies on water splitting catalysts. We are now designing and constructing a light illumination system for the same electron microscope so that we can perform *in situ* and *operando* studies on photocatalytic water splitting materials. We have also completed construction of the first phase of an *ex situ* water splitting test reactor for testing novel photocatalysts. This is a critical step for testing materials that will be suitable for *in situ* and *operando* TEM studies of photocatalyst. (2) Structure-Reactivity Relations – We have completed a series of experiments on titania and tantalate based systems for solar water splitting. These two semiconducting oxides are functionalized with Ni/NiO core-shell structures which serve as water reduction and oxidation sites. We found that for the tantalate-based systems, increasing the thickness of the NiO shell increases the hydrogen production rate by almost a factor of 4 due to suppression of the back reaction. The core-shell structure gradually degrades and this is correlated with a reduction in the hydrogen production. For the titania based system, the activity is much lower and is associated with a photochemical reaction between the Ni metal and OH radical. The core-shell structure changes due to the Ni component undergoing photocorrosion into solution. (3) Vibrational Spectroscopy in the TEM – We have been able to detect vibrational excitations in the transmission electron microscopy for the first time using monochromated electron energy-loss spectroscopy. We have successfully observed optical phonons and molecular vibrational signatures on the surfaces of nanoparticles.

Tomographic Techniques for Electron Microscopy Vector Field Reconstructions

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Students: 0 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding: \$109,000 (2014)

PROGRAM SCOPE

In this project, we explore the use of forward modeling techniques in combination with Lorentz and STEM diffraction contrast transmission electron microscopy observation modes to determine quantitatively the 3-D spatial variations of vector-type physical quantities, such as magnetization and lattice displacement, and derived quantities, such as the magnetic vector potential and lattice strain, in modern engineering materials. The recent availability of spherical aberration correction combined with Lorentz transmission electron microscopy (LTEM) at both Carnegie Mellon University (CMU) and the Argonne National Laboratory (ANL) as well as at the Center for Electron Microscopy and Analysis at the Ohio State University (OSU) opens the door to quantitative 3D high resolution studies of both magnetic material systems and complex microstructures in materials of importance for power generation and propulsion. We build upon our earlier work in vector field electron tomography to expand the

reconstruction of 3D vector fields to the case of displacement fields in multi-phase engineering materials. We aim to create a framework for the forward modeling of tomographic image series which will be capable of dealing with both Lorentz and defect contrast images. This will then allow us to integrate the forward models with model-based tomographic reconstruction algorithms that are currently being developed. This program will result in an efficient, modular, accurate, iterative tomographic reconstruction technique, which can be used for the reconstruction of 3D vector fields, in particular magnetization and defect displacement fields. Our work will lay the foundation for the eventual routine determination of 3D vector fields by TEM techniques.

FY 2014 HIGHLIGHTS

We have created a flexible numerical approach that allows us to consider a magnetic sample as a superposition of magnetized spheres, whose projections can then be superimposed to obtain the magnetic phase shift for an arbitrary magnetization configuration. This approach allows us to create an accurate forward model that will be part of the model-based iterative reconstruction (MBIR) approach for vector field electron tomography. We have also created a flexible algorithm for the numerical simulation of STEM diffraction contrast images of defects in thin foil samples; this algorithm will form the basis for a new MBIR algorithm that will eventually allow us to reconstruct the 3D displacement field around lattice defects,

EARLY CAREER: In-situ TEM Observations of Degradation Mechanisms in Next-Generation High-Energy Density Lithium-Ion Battery Systems

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Funding: \$150,000 (2014)

PROGRAM SCOPE

This project seeks to characterize nanoscale processes associated with the degradation of next-generation high energy density lithium-ion battery electrodes via in-situ transmission electron microscopy (TEM). Dynamic processes active in the electrodes, electrolyte, and intervening interfaces, which are chemical, electrical, and mechanical in nature, have been correlated with capacity fade in lithium ion batteries. Absent direct observation with high spatial, temporal, chemical, and crystallographic resolution, limited understanding of the complex interactions occurring between these multiple processes may be derived. This work will develop a fundamental understanding of degradation mechanisms in representative environmental conditions using commercial electrolytes and electrode designs that mimic commercial electrodes, as well as in idealized solid-state batteries that will enable in-situ atomic-resolution imaging. The research will also develop the experimental techniques necessary for investigating electrochemical systems by in-situ transmission electron microscopy and will provide a framework for distinguishing and limiting electron beam effects that could potentially influence experimental results.

FY 2014 HIGHLIGHTS

In-situ electron microscopy was used to demonstrate unambiguously, for the first time, that power-law deformation creep dominates the mechanical response of high capacity alloying electrodes based on low melting temperature systems, such as Sn-Li, Al-Li, etc. The insight was gained through the ability to dynamically track the local strain rate during lithiation of individual particles and correlate this with the critical condition for particle fracture. Similar studies have found that the fracture behavior of lower diffusivity materials such as Si is insensitive to strain rate. Until now, the importance of lithiation rate on fracture of high capacity electrodes has not been appreciated or reported in the community, and the insight provides new opportunities to engineer failure resistant high capacity electrode materials. Related in-situ TEM techniques were also utilized to study dealloying in model Cu-Au systems that are similar to prior work, completed in this project, investigating dealloying of Li-Sn. The results enable us to understand the role of microstructure in affecting porosity evolution during dealloying, and also provide additional insights into the role of surface diffusion in mediating strain relaxation, which shares similarity with the power law creep described above. The project also contributed to the development of in-situ TEM techniques. We designed, fabricated, and tested the first in-situ environmental TEM platform with low temperature capability. We demonstrated the platform in experiments characterizing phase selection during ice crystallization, but it can be similarly applied to characterizing battery cycling at low or high temperatures relevant to real world applications.

EARLY CAREER: the Nature of the Spin Dependent Surface Chemical Bond: Spin Polarized STM Studies of Metal-Organic Interfaces

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Funding: \$150,000 (2014)

PROGRAM SCOPE

New approaches to spin electronics envision using organic molecular films to control spin polarized carrier flow in devices. This requires the creation of interfaces between organic molecular solids and magnetic electrodes. The spin-dependent electronic coupling at such interfaces is a challenging problem not easily amenable to computational modeling. This project applies sophisticated spin polarized scanning tunneling microscopy and spectroscopy to directly measure the spin-dependent electronic coupling in concert with single molecule imaging. Attention is focused on organic semiconductors interacting with traditional magnetic metal electrodes as well as with more exotic substrates such as magnetic oxides and topological insulators. Important topics include whether covalent chemical bonds are created between the substrate and the molecule, which molecular orbitals are involved in interactions, and to what extent orbitals can be spin polarized by interacting with spin-split substrate states. The end goal is to identify the most important spin-dependent interactions at typical interfaces of interest for the emerging technology of organic and molecular spintronics.

FY 2014 HIGHLIGHTS

In 2014, the project reconstructed the spin polarized STM instrument for more rapid experimental throughput. This included upgrades to sample and tip preparation and particularly the development of bulk Cr tips that can be extensively processed during the experiment to optimize magnetic contrast in the microscope. In addition, we identified the importance of considering magnetic surface states in understanding coupling to molecules. This was particularly evident in our observations of a remarkable long range and indirect coupling between a magnetic surface state on a Cr substrate and the molecular orbitals in an organic semiconductor, PTCDA. This situation arises when the molecule couples to the non-magnetic sp bulk band that determines indirectly the lifetime of the magnetic surface state. Such a subtle effect indicates new complexities in organic spintronic interfaces and new opportunities for designing interfacial interactions by indirect means. Related to this topic of magnetic surface states was our exploration in FY 2014 of the coupling of molecules to topological insulators with spin textured surface states. These states have been recently identified as promising for spintronic applications and we think that molecular films may be valuable for spin injection. Beyond this, we also realized that specific predictions related to the breaking of time reversal symmetry with magnetic molecules can be tested with our spin polarized scanning tunneling microscope. In FY 2014, we learned to create and image topological insulators and made initial explorations of molecular film growth that are important for doping control.

EARLY CAREER: Quantum Control of Spins in Diamond for Nanoscale Magnetic Sensing and Imaging

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Funding: \$150,000 (2014)

PROGRAM SCOPE

The goal of this research is to develop a magnetic field imaging technique with nanoscale resolution that would allow for non-invasive, non-destructive probing of a variety of important physical phenomena such as quantum tunneling in single molecule magnets and quantum bits encoded into spins in quantum dots. Diamond single spin magnetic sensors are a highly promising material platform featuring high magnetic field sensitivity, nanometer spatial resolution and the important ability to operate under ambient or harsh environmental conditions required to study many material systems. The proposed work will take a multi-faceted approach toward improving the accuracy, sensitivity and robustness of this platform through a unique combination of fundamental investigations into quantum control and precision quantum metrology coupled tightly to innovative design, sophisticated nano-fabrication and advanced measurement techniques.

FY 2014 HIGHLIGHTS

Our group had invented a method for achieving accurate high dynamic range magnetometry with a precision beyond the shot-noise limit and showed significant improvement for both DC and AC fields through the use of novel quantum phase estimation algorithms (PEAs). Our latest experimental results were published in Phys. Rev. B (Rapid Comm.), and our theoretical analysis exploring both DC and AC

field sensing with PEAs was published in Phys. Rev. B. Both papers are also available on the arxiv pre-print server. We have carried out new experiments to explore the possibility of using geometric phase rather than dynamical phase for magnetic sensing, and for other applications such as gyroscopes. These results mark the first observation of geometric phase in a single solid-state spin system. The paper is available on the arxiv pre-print server.

EARLY CAREER: Time-resolved electrical, optical, and thermal probes of topological spin textures in magnetic nanostructures

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Funding: \$750,000 (2014-2018)

PROGRAM SCOPE

The goal of this program is to investigate the dynamics of topological spin textures in chiral magnetic systems using a combination of electrical, optical and thermal probes. Nanoscale magnetic configurations with a non-zero topological winding number, also known as magnetic skyrmions, are of particular interest because they are expected to be protected from magnetic pinning defects and they can be moved under tiny applied currents through spin-transfer torques. Additionally, theory suggests unusual dynamical properties for individual skyrmions, including response to an electrically-driven Magnus force and behavior as a massless Dirac particle. Taken together, these topological spin textures are interesting for fundamental science and potentially as a platform for ultra-low power memory and logic devices. One challenge for this research is that magnetic materials that support stable skyrmion phases have a strong Dzyaloshinskii-Moriya interaction. This interaction is achieved in the bulk with a non-centrosymmetric crystal structure such as B20 chiral magnetic materials, or at interfaces between heavy metals and conventional magnetic materials. This program seeks to experimentally develop skyrmion containing magnetic materials and probe their behaviors using a combination of high-frequency magneto-transport, magneto-optical microscopy, magneto-thermal microscopy, and high resolution Lorentz contrast transmission electron microscopy (LTEM). We focus on understanding dynamics of individual skyrmions in magnetic nanostructures using a combination of techniques to access the relevant short length and time scales.

FY 2014 HIGHLIGHTS

This program was launched in summer of 2014. In that time we have made progress on two fronts. In the first, we have been developing a fabrication procedure capable of making lateral magnetic nanostructures with electrical contacts that are compatible with LTEM imaging. In the second, we have been developing the material synthesis of B20 chiral magnetic materials. We have succeeded in growing B20 phase FeGe thin films on Si [111] using a combination DC magnetron co-sputtering and thermal annealing. These films have been characterized using x-ray diffraction and found to be single crystal.

Polarization-Coupled Tunable Resistive Behavior in Oxide Ferroelectric Heterostructures

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Funding: \$246,338 (2014)

PROGRAM SCOPE

The main objective of this research is investigation of the physical mechanism of the electrically and mechanically tunable nonvolatile resistive behavior in oxide ferroelectric heterostructures with engineered interfaces realized via a strong coupling of ferroelectric polarization with tunneling electroresistance and metal-insulator (M-I) transitions. This proposal builds up on the breakthrough scientific results achieved during the previous DOE-supported research, which include: (1) observation of electrically tunable low-resistance state in ferroelectric tunnel junctions (FTJs); (2) demonstration of voltage-free ferroelectric and resistive switching induced by application of a localized mechanical stress gradient; (3) demonstration of a new mechanism of electrical control of 2D electron gas (2DEG) at oxide interfaces related to a switchable electrically-induced polarization in nominally non-ferroelectric oxide layers. The research goals will be achieved by creating strong synergy between cutting-edge fabrication, characterization and modeling capabilities. Extensive expertise of the PIs team (Gruverman, Eom and Tsymbal) creates a unique combination of complementary cutting-edge research approaches and provides the best opportunity for ensuing success. Using theoretical predictions, the project will identify perspective materials and structures for implementation of tunable resistance by electrical and mechanical stimuli. Furthermore, the concept of the ferroelectric junctions with electrically and mechanically tunable nonvolatile resistance represents a new paradigm shift in realization of the next-generation of non-volatile memory devices and low-power logic switches.

FY 2014 HIGHLIGHTS

Ferroelectric Tunnel Junctions with Graphene Electrodes We demonstrated a first use of graphene as electrodes in ferroelectric tunnel junctions (FTJs) – bistable resistance devices, where switching from the low (ON) to the high (OFF) resistance states is controlled by electrically induced polarization reversal. FTJs have a high potential for use in nonvolatile memory and logic devices due to their speed and low power consumption. The developed approach provides a simple and straightforward method for significant enhancement of the FTJ performance, i.e. its retention and OFF/ON ratio. A key concept of our work is introduction of a molecular layer at the graphene/ferroelectric interface by transferring graphene in different solvents on the surface of the ultrathin ferroelectric BaTiO₃ film. We show that polarization stability and resistive switching behavior of the FTJs are strongly affected by the molecular structure of this layer. Specifically, we find that the interfacial ammonia layer results in strong polarization retention and boosts the OFF/ON resistance ratio by almost three orders of magnitude. The reported results were published in Nature Communications 5, 5518 (2014).

Understanding Microscopic Mechanism of Spin Pumping and Magnetization Dynamics in Novel, Tailored Magnetic Material

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Sr. Investigator(s):

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Funding: \$185,000 (2014)

PROGRAM SCOPE

Spin pumping—the transport of spin angular momentum into neighboring material from a ferromagnet (FM) driven out of equilibrium by microwave excitation—is receiving a great deal of attention because of its potential technological importance and the richness and breadth of the science involved. A powerful diagnostic for spin pumping is the transfer of energy from the precessing magnetization that accompanies the angular momentum transport. This energy transfer is evident in measurements of the damping of the mode, damping which is in addition to the better understood intrinsic damping. This damping is unusual because it is non-local making it an exciting scientific topic in its own right. The mechanisms underlying conventional, local damping, including Gilbert-damping and spin wave emission in isolated FM films, have been extensively studied. Non-local damping is associated with transfer of angular momentum to an adjacent non-magnet (NM) layer. There is now broad agreement that spin pumping (transfer of angular momentum) and enhanced damping are two aspects of the same phenomenon and their relationship has been studied in metallic FM/NM bilayer and multilayer systems in which itinerant electrons interact across an abrupt interface. However, a quantitative description of the dependence of the spin-mixing conductance, the key parameter that quantifies spin pumping and non-local damping, on microscopic characteristics of the interface is lacking. Beyond this, and contrary to expectations from models, experimentally determined values of the spin mixing conductance are found to vary only slightly across a large variety of disparate FM and NM materials ranging from metals to semiconductors to insulators. We are studying these phenomena using microscopic scanned probe techniques and with magnetic-field defined boundaries that avoid complexities associated with material interfaces.

FY 2014 HIGHLIGHTS

Our multi-pronged approach to understanding the mechanisms by which angular momentum is transferred from the excited magnetization of a ferromagnet into adjacent material has generated 8 publications including 3 in Physical Review Letters. Using FMR spin pumping we have extensively studied the transport of spin through a variety of materials by means of the inverse spin Hall effect (ISHE) and measured the damping of the magnetization that arises specifically in association with these spin currents, and we have used FMR microscopy to study spin transport from microscopically confined spin wave modes in the absence of any material interfaces. Our scanned probe FMR measurements of the damping of spin wave modes confined solely by a strong, local magnetic field gradient have observed non-local damping. This damping is due to the transfer of angular momentum, that is spin pumping, from the confined mode into the ferromagnetic material in the surrounding film which serves as an equilibrium spin reservoir. We have explored spin transport through materials ranging from insulating oxides to transition metals to insulating ferromagnets and antiferromagnets. These studies reveal the sensitivity of spin transport to details of the interface and to the magnetic character of the material itself. We observed 1000-fold exponential decay of spin pumping across insulating barriers underscoring the importance of exchange coupling at the interface. In studies of diverse 3d, 4d and 5d metals we determined interfacial spin mixing conductances from measurements of Gilbert damping enhancement and ISHE to show that the spin Hall angle is dominated by the sensitivity of the d-orbital moment to the d-electron count. Our study of spin pumping into FM metals, including Py, Fe, Co, and Ni, revealed a high

effective spin mixing conductance. We discovered strain tuning of magnetocrystalline anisotropy over a range of more than 1000 G in epitaxial YIG films.

Switching in Solid State Memories via Nucleation and Growth Mechanisms: Causes and Effects at the Nanometer and Nanosecond Scale

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

The development and optimization of applications comprising functional materials necessitates a thorough understanding of their static and dynamic properties and performance. While many experimental techniques are employed for such studies, high speed scanning probe microscopy is particularly suitable as it provides nanoscale maps of topographic features with simultaneous measurement of local functional properties. Leveraging such High Speed SPM and concepts enabled by it, efficient measurements and maps with nanoscale and nanosecond temporal resolution are thus uniquely feasible. This includes recent enhancements for topographic, conductivity, ferroelectric, and piezoelectric properties as originally proposed, as well as newly developed improvements to AFM-based mechanical, thermal, and photoconductivity maps. These capabilities are employed to gain novel insight into energy-efficient data storage systems such as phase change and ferroelectric memories, to map the influence of defects in energy-generation systems such as solar cells, and to guide the development of a new class of magnetoelectric switching for magnetic field sensing and data storage.

FY 2014 HIGHLIGHTS

A widely applicable modification to AFM imaging was devised that can greatly improve the accuracy of topographic and property maps, simplify AFM training and operation, and enable high speed AFM imaging even on legacy systems (Bosse et. al., *Nanotechnology*, 25, 2014). This is based on summing the traditionally measured height from AFM topography measurements with calibrated deflection (or amplitude) signals. These corrections have been overlooked essentially since AFM was invented more than 25 years ago. With suitable additional calibration steps, they are further shown to be applicable for improvements in a wide variety of property mapping variations of AFM. Leveraging high-speed imaging capabilities, multidimensional imaging with SPM was also widely implemented for mapping functional properties in phase change materials, microfabricated devices, and photovoltaics. This includes novel thermal characterization (Tovee, *JAP*, 116, 2014), ultrasound based mechanical modulus mapping (Bosse et. al., *JAP*, 115, 2014), friction mapping (Bosse et. al., *MST* 25, 2014), and conductance in photovoltaics (Kutes et. al., *Prog. Photovoltaics*, submitted, 2014). The first direct evidence of ferroelectric domains in the new class of solar cells known as perovskite thin films was also reported for polycrystalline MAPbI₃ thin films (Kutes, *J. Phys. Chem. Lett.*, 5, 2014). Multiferroics were intensively investigated as well, particularly the behavior of ferroelectric domains in poly-domain epitaxial films. This statistically revealed and spatially resolved full ferroelectric polarization reversals occurring via multiple ferroelastic switches. When coupled with overlaying ferromagnetic thin films, this allows previously

unexpected deterministic switching of magnetic domains, demonstrated with efficient room temperature control of spin valve states (Heron et. al., Nature, 516, 2014).

Vortex Matter in Confined Superconductors and Mesoscopic Hybrid Heterostructures

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Funding: \$200,667 (2014)

PROGRAM SCOPE

The primary emphasis of this project is on the physics of vortices in confined superconductors and hybrid heterostructures such as superconductor-ferromagnet (S/F) systems. The goal is to understand how the physics of vortex matter changes in order to be able to predict and control the electronic properties of new hybrid systems. Vortices in superconductors can be probed with high spatial resolution by mapping the spatial variations in the electronic density of states with Scanning Tunneling Microscopy. The proposed program is divided in two parts. The first part focuses on studying the emergence of superconductivity and vortex matter in mesoscopic superconductors. Properties of superconducting materials differ greatly from the bulk properties when the size of the sample is small (compared to the coherence length and the London penetration depth). Critical parameters such as critical current and critical field can be greatly enhanced and the vortex configuration can be strongly influenced by the sample geometry. Despite many efforts over the last decade some fundamental issues are still open. In particular, we are still lacking a description of the emergence of superconductivity at the nanoscale. The second part of this program focuses on the investigation of hybrid nanostructures incorporating superconducting and ferromagnetic components. Understanding of the physics involved will be combined with searching novel guiding principles to enhance materials and devices functionalities by combining specific properties of ferromagnets and superconductors. In proximity coupled structures the interplay between magnetism and superconductivity leads to new physical phenomena with superconductivity coexisting with ferromagnetism at the interface. In magnetically coupled structures the stray field of the ferromagnet leads to an inhomogeneous superconducting state where superconductivity and vortices can be confined in channels determined by the underlying magnetic template.

FY 2014 HIGHLIGHTS

Magnetically coupled planar ferromagnet-superconductor (F/S) hybrid structures offer new avenues for manipulation of the superconductivity at the nanoscale and convenient means to control vortex dynamics. The nonuniform magnetic field produced by the ferromagnet spatially confines superconductivity. When the temperature is decreased below the superconducting critical temperature, the superconductivity nucleates first at the location where the stray field is minimum, i.e. at the domain wall, which is a realization of domain wall superconductivity. Therefore, the superconductivity is confined in tiny channels that can more or less interact depending upon the distance between them. These channels can be positioned at different locations in the superconductors by applying an external magnetic field. These effects known as domain wall superconductivity and reverse domain superconductivity were theoretically predicted and inferred experimentally only by global

measurements. Our measurements provided the first direct visualization of the nucleation of the superconductivity in regions above the domain walls. Moreover, we demonstrated that such F/S structures are attractive model systems that offer the possibility to control the strength and the location of the superconducting nucleus by applying an external magnetic field. We fabricated F/S structures consisting of Co-Pd multilayers having different stripe domains width and we found that the nucleation of superconductivity at the domain wall is critically dependent upon the domain width. Indeed, if the domains are too narrow the superconducting nuclei overlap and the superconductivity will nucleate everywhere with slight spatial inhomogeneity.

High-Resolution Photoemission Electron Microscopy on Femtosecond Time Scales

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Funding: \$210,000 (2014)

PROGRAM SCOPE

The project seeks to improve the capabilities of photoemission electron microscopy (PEEM) through aberration correction and utilize these improvements in non-linear optical studies of surfaces at femtosecond time scales. A new electrostatic aberration corrector capable of simultaneous correction of chromatic and spherical aberration has been designed and is being tested and used in this project. A new approach for the determination of aberration coefficients for PEEM is developed to provide optimized corrector settings during microscope operation. The improved imaging capabilities are applied to microscopy work on ultrafast time scales. PEEM uses photo-excited electrons to generate electron micrographs from sample surfaces. In our case femtosecond multi-photon emission processes are utilized to study photon and plasmon dynamics. The goal of this work is to explore possibilities for a coherent control of the optical response in metals and transparent conductive media. The ultrafast imaging capabilities in PEEM allow us to stay within the coherence times of typical surface plasmon systems and hence study coherent control. With the direct (i.e. non-scanning) imaging capabilities in PEEM an in-situ approach appears possible and will be pursued. A detailed analysis of the correlations between optical input and sample response will allow us to establish guidelines and rules for this type of optical control. Aberration correction in this work is needed to bring the resolution into the true nanometer range and to obtain sufficient contrast at experimental photoemission yields which are customarily low.

FY 2014 HIGHLIGHTS

In the past year we have successfully developed a new method to determine the aberration coefficients in real-time, i.e. during the microscopy work on a given sample. This method is combined with a simulation-based procedure to deliver optimized corrector settings for that sample. In essence, the new method will render aberration correction in PEEM much more practical and also more precise. With further fine-tuning of the method we expect further resolution improvement in the near future. The instrument-related work on the microscope has significantly enhanced our experimental approach to image and analyze the optical response of surfaces. Using aberration correction we are now able to image photon and surface plasmon distributions at solid surfaces with a resolution of ~15nm.

Furthermore, with a two-dimensional modelling approach based on a Green's function method we are able to establish a precise simulation of the experimentally obtained images. From the comparison between simulated and experimental data we can extract the optical parameters in nanostructures on a similar spatial scale as given by the image resolution. With this information the dynamic interaction of plasmons and photons can be quantitatively evaluated, energy transfer and dissipation, coherence loss and other interactions can be analyzed directly from the images. Examples of coherent surface plasmon control have also been successfully established: In a ring-shaped gold/copper antenna of sub-micron dimensions we demonstrated, for the first time, precise and predictable position control for a localized surface plasmon resonance. Such control will be useful in many applications. Overall, our work shows quite clearly an emergent potential for applying electron imaging to light optics and plasmonics. In this project we literally observe light with electrons.

EARLY CAREER: Microscopy of Electrostatic Field Effect in Novel Quantum Materials

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Funding: \$150,339 (2014)

PROGRAM SCOPE

The objective of this research is to explore the nanoscale electronic properties when charge carriers are electrostatically modulated in advanced quantum materials, such as complex oxides, layered chalcogenides, and organic semiconductors. By combining novel methods such as ferroelectric or electrolytic gating with scanning microwave impedance microscopy that probes sub-surface phenomena, this project aims to establish a new type of useful imaging methodology as well as to answer many key questions on technologically important materials. Specifically, the research will spatially resolve electronic phase transitions induced by density modulation, compare the underlying physics between bulk chemical doping and surface electrostatic doping, and investigate the microscopic origin of sub-threshold behaviors in various field-effect transistors.

FY 2014 HIGHLIGHTS

The microwave impedance microscope (MIM) is capable of detecting the nanoscale conductivity distribution in the buried semiconductor-dielectric interface through capacitive coupling. We have demonstrated the carrier density modulation at the strained BaTiO₃-Ge interface when the polarization is switched by the tip bias. To our knowledge, this is the first time ferroelectric field effect is reported on semiconductors. We have also studied electric-double-layer transistors (EDLTs) using electrolytes as gate dielectrics. Our results on ZnO substrates showed the metal-insulator transition in the EDLT structure with an ultra-thin (about 50nm) ion gel film. At the same time, successful MIM conductivity imaging has been demonstrated below the glass transition temperature of 200K. With instruments successfully installed and preliminary data obtained, we expect to enter an exciting and unexplored regime through the unique MIM measurements.

Scanning Quantum Gas Atom Chip Microscopy of Strongly Correlated and Topologically Nontrivial Materials

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Funding: \$450,000 (2014-2016)

PROGRAM SCOPE

Microscopy techniques co-opted from nonlinear optics and high energy physics have complemented solid-state probes in elucidating exotic order manifest in condensed matter materials. Up until now, however, no attempts have been made to use modern techniques of ultracold atomic physics to directly explore properties of strongly correlated or topologically protected materials. We will continue to develop the SQCRAMscope, a novel Scanning Quantum Cryogenic Atom Microscope technique for imaging magnetic and electric fields near cryogenically cooled materials. With our SQCRAMscope, we aim to image inhomogeneous transport and domain percolation in technologically relevant materials whose order has evaded elucidation.

FY 2014 HIGHLIGHTS

Our new DOE funding began at the end of FY 2014, so we don't have as much to report as we will for FY 2015, but we can state that we have pushed the resolution of the microscope to below 1 um and increased the robustness of the BEC production apparatus. We are working on a manuscript reporting our characterizations of the sensitivity and resolution of the SQCRAMscope.

Tailoring the Electronic Properties of Graphene via Nanostructuring: An Integrated Atomic Resolution STM and Non-Contact AFM Study

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Funding: \$186,000 (2014)

PROGRAM SCOPE

The underlying theme of the project is the study of graphene in the presence of confinement and varied boundary conditions. A necessary step is the preparation of nanostructured graphene. Work carried out during the current DOE support has demonstrated the feasibility of several routes for nanostructuring graphene, including Fe nanoparticle assisted hydrogen etching, and the growth of quantum dots on epitaxial graphene SiC. The formation of nanostructures of this 2D material necessarily leads to the existence of edges with significantly modified electronic properties. Edge states and energy level quantization are the intrinsic and interrelated consequences of the broken symmetry and quantum confinement. As the inherent boundaries of graphene quantum dots, edge structures impose potentials

that vary at the nanometer scale, representing a model system to explore relativistic quantum systems in condensed matter experiments under conditions unreachable for truly massless particles. The proposed research in the edge stability and reconstruction will lead to new discoveries in graphene such as chaotic energy level quantization, edge spin-polarization, and Anderson localization induced by edge disorder. Furthermore, our research addresses the pseudo-magnetic fields associated with the strained graphene nanostructures. To tackle these challenging tasks, a highly interactive team has been assembled, integrating the Pls' strengths in material synthesis and imaging (Li) and calculations (Weinert). With our *in situ* growth capability, unique combination of low-temperature atomic resolution STM and AFM, accompanied by density functional theory calculations, we are well positioned to conduct this research. The successful execution of the research plan will expand our knowledge base of the exotic properties and potentially enhanced functionalities of graphene, a material system that may significantly impact the fields of nano electronics and spintronics.

FY 2014 HIGHLIGHTS

During this 2014 budget period, (1) We have fabricated and demonstrated tunable bandgaps in semiconducting zigzag nanoribbons with hydrogen edge termination. (2) We have demonstrated for the 1st time metallicity in O-terminated zigzag nanoribbons. (3) We have shown that fluctuations in Schottky barrier height at the graphene-semiconductor (SiC, Si, and GaAs) junctions are directly related to the spatial and charge density variations in the graphene layer. (4) We have theoretically investigated the impact of Ag substrate on the band structure of silicene, a Si analog of graphene. (5) We have determined the atomic structure of graphene grain boundaries. These findings have led to the following publications: 1. (cover article) "Determining charge state of graphene vacancy by noncontact atomic force microscopy and first-principles calculations", Y Liu, M Weinert and L Li, *Nanotechnol.* 26, 035702 (2015). 2. "Direct experimental determination of onset of electron-electron interactions in gap opening of zigzag graphene nanoribbons", Y. Y. Li, M. X. Chen, M. Weinert, and L. Li, *Nat. Commun.* 5:4311 doi: 10.1038/ncomms5311 (2014). 3. "Transport and photoconduction characteristics of metal-graphene-4H-SiC(0001) heterojunction devices", T. Hosseini, D. Tomer, S. Rajput, L. Li, and N. Kouklin, *Appl. Phys. Lett.* 105, 223107 (2014). 4. "Intrinsic inhomogeneity in barrier height at monolayer graphene/SiC Schottky junction", D. Tomer, S. Rajput, L. J. Hudy, and L. Li, *App. Phys. Lett.* 105, 021607 (2014). 5. "Revealing the substrate origin of the linear dispersion of silicene/Ag(111)", M. X. Chen and M. Weinert, *Nano Lett.* 14, 5189 (2014). 6. "Direct experimental evidence for the reversal of carrier type upon hydrogen intercalation in epitaxial graphene/SiC(0001)", S. Rajput, Y. Y. Li, and L. Li, *Appl. Phys. Lett.* 104, 041908 (2014).

STM Studies of Spin-Orbit Coupled Phases in Real- and Momentum-Space

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PROGRAM SCOPE

The recently discovered class of spin-orbit coupled materials with interesting topological character is fascinating both from a fundamental as well as an application point of view. One striking example is the

class of materials called 3D topological insulators (TIs). These materials host linearly dispersing (Dirac like) surface states with an odd number of Dirac nodes and are predicted to carry a quantized half-integer value of the axion field. The non-trivial topological properties of TIs arise from strong spin-orbit coupling leading to an inverted band structure; which also leads to the chiral spin texture in momentum space. In an entirely different class of topological systems, (MnSi, or Fe/Ir(111) for example) similar chiral spin texture in the form of Skyrmions is observed, but in real space. In this proposal we describe our plans to use low temperature scanning tunneling microscopy (STM) and spectroscopy (STS), back-gated STM, and spin-polarized STM to study materials with topological phases in real- and momentum-space. The materials we propose to study include 3D topological insulators, Skyrmion systems and 2D topological insulators. Using low temperature scanning tunneling spectroscopy and related techniques, our objectives answer fundamental questions such as: What is the influence of the position of the Fermi energy on the properties of topological insulators doped with magnetic and non-magnetic impurities? How far does the single particle picture apply? What are the new phases that emerge as correlations are strengthened? What are the consequences of electron-phonon coupling on the prototypical 3D TIs Bi_2X_3 ($\text{X}=\text{Se}, \text{Te}$)? How do we realize 2D topological insulators in mono- or bi-layer thin films? Can we see the edge modes in 2D topological insulators? In addition, we will use our techniques to visualize and uncover the physics of interesting new phases in topological materials such as: Landau level stripes, quantum spin Hall effect, and 1D chiral spin modes.

FY 2014 HIGHLIGHTS

A fundamental property predicted for topological crystalline insulator (TCI) family of materials is that due to symmetry constraints the orbital character of the surface state (SS) bands is different above and below the Dirac point. Both orbital- and spin-texture are therefore essential for a complete description of the TCI SS band structure. To experimentally probe this, we measured the interference patterns of $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$ in the topological regime by scanning tunneling spectroscopy (STS). We find that the intensity and energy dependence of the FTs show distinct characteristics, which by comparison with theory can be attributed to orbital effects. Another central question in the field of topological insulators involves the fate of the Dirac surface states when band inversion is undone and the material becomes non-topological. Here, we use scanning tunneling microscopy to track the quantum phase transition in a topological crystalline insulator (TCI), $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$, tuned by Sn content. We discover the existence of surface states in the trivial phase that have the characteristics of gapped, double-branched Dirac fermions. We demonstrate how these states induced by proximity to the topological phase, morph into robust topologically protected Dirac surface states across the critical composition. In a different study we developed a new technique to characterize electron-phonon coupling using Landau level spectroscopy. Quantifying the interaction between phonons and electrons is of immense importance for complete understanding of materials. Nearly all information about electron-phonon coupling (EPC) is contained in the Eliashberg function of the material, but its precise extraction has in part been limited due to the lack of local experimental probes. In this work, by utilizing Landau level spectroscopy, we construct a method to directly extract the Eliashberg function, and demonstrate its applicability to lightly-doped thermoelectric bulk insulator PbSe.

New Methods of Imaging Surfaces

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PROGRAM SCOPE

Oxide surfaces are an important frontier, with numerous energy-related applications in areas ranging from catalysis to the emerging field of oxide electronics. Despite this, our understanding of the atomic structure of oxide surfaces is relatively primitive and it is hard to probe in detail the local atomic structure with available experimental tools. It has recently become apparent that the latest generation of aberration corrected transmission electron microscopes can image oxide surfaces in plan view with signals which are surprisingly strong and with resolutions of at least 1.5 Angstroms and probably better. It is also possible to obtain surface images not just using conventional high-resolution imaging, but also with annular dark-field and by detecting secondary electrons, again with atomic resolution. The focus of this research is to exploit this type of imaging information to improve the understanding of oxide surfaces, using both the unique UHV microscope at Northwestern University as well as advanced microscopes elsewhere in the US. This will involve both developing the methods as a tool as well as exploiting the information to solve surface structures previously unsolved (and perhaps unsolvable by existing techniques). The imaging information will be combined with other information, including direct-methods analyses based upon the use of transmission electron diffraction data, surface chemical analyses using XPS and advanced density-functional calculations including exact-exchange hybrid methods and more chemical approaches such as bond valence analyses. The last two provide energetic and chemical information which is central to understanding the thermodynamics and kinetics factors determining which surface structures form. A longer-term aim is to develop the methods so they can be used to obtain local information from the surfaces of inhomogeneous nanoscale objects such as SrTiO₃ nanocuboids.

FY 2014 HIGHLIGHTS

This period has seen substantial progress in a number of areas: 1) For SEM imaging of surfaces we now understand the details of what matters, what does not and there are some surprises such as an unexpected importance of dielectric screening at the surface. 2) We have now determined in some detail what matters for obtaining HREM images of surfaces in plan view, better than the early work from more than a decade ago. Modern aberration corrected microscopes matter. 3) We have solved quite comprehensively a large set of structures on the SrTiO₃ (111) surface including a new approach to understanding them based upon a Potts model approach. 4) We have determined a new range of structures on the SrTiO₃ (110) surface joint with collaborators in the UK and Austria. 5) We have broken new ground with KNbO₃ and NdGaO₃, oxides of technological importance for thin film growth about which nothing was previously known.

EARLY CAREER: Electron Microscopy with Vortex Beams Carrying Orbital Angular Momentum

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Funding: \$150,000 (2014)

PROGRAM SCOPE

The goal of this project is to use a novel type of electron beam carrying quantized orbital angular momentum for new electron microscopy capabilities. The electron vortex beam is composed of free electrons with helical wavefunctions, analogous to optical vortices in beams of light (also known as twisted light). Unlike light, electron vortex beams also have unique magnetic properties, can be focused to atomic dimensions, and can interact with matter in unique new ways. The beams can be generated in conventional electron microscopes using a new technology: coherent electron wavefront engineering using nanofabricated diffraction holograms. This provides a way to upgrade existing instruments with electron vortex probe beams. In this project the unique orbital angular momentum, helical phase, and magnetic properties of the electron vortex will be applied to image magnetic and biological materials with unprecedented resolution using existing electron microscopes. The major objectives of the project are to (1) develop and refine diffractive electron optics for use in existing microscopes, (2) apply this new technology to image magnetic phenomena at nanometer length scales and below using scanning transmission electron microscopy (STEM) with vortex probe beams, (3) image low-scattering, normally-transparent soft materials in (S)TEM using electron vortex spiral phase filtering to provide enhanced contrast, and (4) explore and develop lower-energy scanning electron microscopy (SEM) capabilities using electron vortex beams.

FY 2014 HIGHLIGHTS

In FY 2014, we completed a study to maximize the diffraction efficiency and quality of nanofabricated diffractive optics for electrons. We wrote and published an article detailing these studies [New J. Phys. 16, 093039 (2014)]. Based on this research, we fabricated a grating for producing electron vortex beams and installed it in the TEAM I instrument at the National Center for Electron Microscopy (NCEM). We used this capability to demonstrate atomic resolution STEM images using a vortex beam [Microsc. & Microanal. 20, 84 (2014)]. After equipping a STEM instrument at University of Oregon with a highly efficient phase grating, we performed low-loss EELS measurements of a vortex beam incident upon spherical gold nanoparticles. We were able to demonstrate transfer of quantized orbital angular momentum from the beam to a surface plasmon resonance in the nanoparticle [Microsc. & Microanal. 20, 68 (2014)]. We also demonstrated initial results of chiral plasmons induced by vortex beams of a particular handedness. This is an initial demonstration of electron dichroism using vortex beams.

In Situ Analytical Electron Microscopy for Probing Dynamic Nano-Scale Electrochemistry

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Funding:	\$180,000 (2014)

PROGRAM SCOPE

In this project, we focus on the development and optimization of *in situ* analytical electron microscopy to quantitatively understand the dynamic changes in the bulk and interfaces of electrodes and electrolytes within all solid state batteries. The objectives of the proposed research are 1) to design and fabricate all solid state batteries with a new electrochemical materials family; 2) to develop the

fundamental understanding of the dynamic chemical and electronic processes at the solid/solid interfaces of electrode/electrolyte; and 3) to make significant inroads towards understanding the basic science of ion transport and related phase transitions in electrochemical systems at the nanometer scale.

FY 2014 HIGHLIGHTS

We have successfully optimized the Focused Ion Beam (FIB) fabrication procedures used to preserve the electrochemical activity of nanobatteries and we succeeded in in-situ TEM biasing of nanobatteries. Through quantitative electron energy loss spectroscopy (EELS) characterizations we observed novel interfacial phenomena at the LiPON/LCO interfaces. We successfully correlate the phenomena to the electrochemical properties of the energy storage solid state batteries. This is the first time such interface phenomena has been observed in all solid state battery. Thin-film $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) as anode material for lithium ion battery was studied using conductive atomic force microscopy (cAFM) in order to elucidate aspects of its reversible phase transition to $\text{Li}_7\text{Ti}_5\text{O}_{12}$ upon cycling. This allows us to directly observe the formation of a percolation network of electronic conductive phase and its eventual deterioration, which may be a possible degradation mechanism not yet reported before. Our work provides critical insights in designing and optimizing the next generation solid state batteries for ultra safe and long life energy storage technology.

Three-Dimensional Characterization of Nanomaterials at Atomic Resolution Using STEM Tomography

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PROGRAM SCOPE

In this project, we propose to perform 3D characterization of nanoparticles at atomic resolution by using scanning transmission electron microscopy (STEM) tomography. Specifically, we will achieve the following three aims in this project. First, we will perform a comprehensive study of the non-linear diffraction and dynamical scattering effects by incorporating multislice STEM calculations into the equal slope tomography (EST) reconstruction. We will also use this simulation study to optimize the experimental parameters, including particle size, particle orientation, material composition, beam energy, defocus, and detector inner and outer angles, for 3D characterization of nanomaterials at atomic resolution. Second, we will develop methods for identifying all atoms in nanoparticles through a combination of high-quality tilt series, the EST reconstruction, 3D Bragg peak filtering and 3D atomic structure refinement. We will first verify the feasibility of locating all atoms in nanoparticles by using multislice simulations, and then optimize STEM experiments to achieve this goal. Third, we will address several outstanding materials science problems by using atomic resolution STEM tomography. Specifically, we will identify all 3D grains in Au nanoparticles at atomic resolution. We will perform 3D characterization of metallic nanocatalysts at atomic resolution, and resolve the location of all atoms and defects in core/shell structured quantum dots. Finally, we have formed an interdisciplinary team including Drs. Ulrich Dahmen and Peter Ercius of the NCEM, LBNL, Profs. Chris Regan and Yu Huang of UCLA, and Prof. Hao Zeng of University of Buffalo. We expect atomic resolution STEM tomography to

significantly expand our fundamental understanding of the structure and functions of nanoparticles and nanomaterials.

FY 2014 HIGHLIGHTS

We made the following accomplishments for the project within fiscal year 2014. First, we performed a series of STEM tomographic experiments on FePt nanocrystals. As synthesized, the FePt nanocrystals exhibit a chemically disordered face-centered cubic (FCC) phase. After thermal annealing at 600°C for ~30 minutes, the nanocrystals change to a chemically ordered face-centered tetragonal (FCT) phase and also show very strong ferromagnetism. A tilt series from an annealed FePt nanocrystal was measured. After performing an EST reconstruction, we performed the element-resolved 3D structure determination of the FePt nanoparticle at atomic resolution. Second, through numerical experiments, we demonstrate an electron tomography method for 3D structural determination of amorphous materials at atomic resolution. By combining multislice simulations of an aberration-corrected STEM with EST, we have determined the 3D atomic structure of a simulated glass particle, consisting of 334 Si and 668 O atoms, from a tilt series of 55 noisy projections. An atomic model refinement method has been implemented to locate the positions of the Si and O atoms in the reconstruction. Finally, we, together with collaborators from Fudan University in China, recently created freestanding atomic silver chains (ASCs) with more than a micrometer long that are suspended in the pores of the hollandite manganese oxide. These ASCs are very stable under ambient conditions with a wide range of temperatures. Our experimental results, including STEM images, indicate that the ASCs have tunable electronic states and exhibit exotic quantum effects such as Peierls distortions. Density functional theory calculations predict that the ASCs have one-dimensional monovalent single-atom quantized conductance.

Structure and Dynamics of Domains in Ferroelectric Nanostructures - *In Situ* TEM Studies

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Funding:	\$185,000 (2014)

PROGRAM SCOPE

The main goal of the proposed research is to explore the structure and dynamic behaviors of ferroelectric domains in ferroelectric thin films and nanostructures by advanced transmission electron microscopy (TEM) techniques in close collaboration with phase field modeling. The experimental techniques used include aberration-corrected sub-Å resolution TEM and in-situ TEM using a novel scanning tunneling microscopy (STM) - TEM holder which allows the direct observation of nucleation and dynamic evolution of ferroelectric domains under applied electric field. Specifically, we propose (1) to study the roles of static electrical boundary conditions and electrical charge in controlling the equilibrium domain structures of BiFeO₃ thin films with controlled substrate constraints, (2) to explore the fundamental mechanisms of ferroelectric domain nucleation, growth, and switching under an applied electric field in both uniform thin films and nanofabricated nanostructures, and to understand the roles of crystal defects such as dislocations and interfaces in these processes, (3) to understand the physics of ferroelectric domain walls and the influence of defects on the electrical switching of

ferroelectric domains. The nucleation and dynamic evolution of ferroelectric domains observed by in-situ TEM under applied external electric field are quantitatively analyzed and directly compared with phase field simulations in Professor Long-Qing Chen's group at Penn State University.

FY 2014 HIGHLIGHTS

(1) Atomic-scale mechanisms of domain wall motion in ferroelectrics: Using unique in-situ TEM techniques, we performed the direct observation of ferroelectric domain wall motion under a probe induced electrical field with atomic resolution. The wall propagates through formation and growth of atomically thin step nuclei, in which the polarization is attenuated. The motion proceeds via a series of discontinuous jumps due to periodic lattice pinning effects. As the wall is moving away from the probe, dynamic transition from rough to smooth in wall motion is observed, along with a change of nucleation and growth rates. These observations coupled with phase-field simulations revealed how local electric fields interact with the lattice potential to enable domain wall propagation. This development offers a powerful means for exploring the physics of many types of topological defects in condensed matter systems. (2) Giant resistive switching via control of ferroelectric charged domain walls: Theoretical and experimental investigations have demonstrated that a quasi-two-dimensional electron gas can form at ferroelectric strongly charged domain walls (sCDWs) that break polarization continuity and enables formation of writable, metallicly conductive channels through the insulating bulk. Control of such sCDWs, however, has been a major challenge due to their instability. Here, using a novel *in situ* transmission electron microscopy combined with phase field simulations, we report controlled switching of resistivity in ferroelectric thin films by writing and erasing stable, nanoscale sCDWs. The switching process occurs through a novel mechanism of a transition between different lattice symmetries. The resistance can be read non-destructively and presents the largest off/on ratio ($\sim 10^5$) ever reported in room temperature ferroelectric devices, opening new avenues for engineering ferroelectric thin film devices.

Physics of Complex Materials Systems Through Theory and Microscopy/EELS

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Funding: \$280,750 (2014)

PROGRAM SCOPE

The main objective is to combine density functional theory (DFT) with Z-contrast imaging and electron-energy-loss spectroscopy, obtained with scanning transmission electron microscopes (STEMs), to elucidate structure-property relations in complex materials structures. A key subtask has been the development of computer codes that combine DFT calculations of electron excitations in solids with dynamical scattering theory that tracks the microscope's finely focused electron beam as it undergoes diffraction in the sample, exits, and gets collected in the detector, including all interference effects. These simulations are aimed at the new capabilities of aberration-corrected STEMs, which provide high-resolution two-dimensional maps of EELS spectral features, generated by collecting probe-position-dependent EELS.

FY 2014 HIGHLIGHTS

A major accomplishment during the present grant period is the joint theory/experiment demonstration that VEELS contains atomic-resolution contrast and thus can rival photon-based spectroscopies, which have low spatial resolution, for the study of complex, inhomogeneous structures. Despite long-held beliefs, based on qualitative arguments, that VEELS would not contain atomic-scale contrast, experimental data on monolayer graphene and matching theoretical simulations demonstrated the existence of atomic-scale contrast. A paper has been submitted for publication. In fiscal 2014, 10 papers have been published in premier journals. Highlights were: (1) A joint experiment-theory demonstration that stable, ultrathin (three atoms across), conducting nanowires can be fabricated in a single sheet of transition-metal dichalcogenides. (2) The discovery of a new form of crystalline order in CuInS₂ nanoparticles. All atoms reside at sites of a perfect lattice, but the Cu and In atoms, which share a sublattice, can order in several distinct ways, forming domains, without any strain or defects. These materials are expected to be suitable for thermoelectric applications. (3) The discovery that Si atoms can passivate nanoscale holes in monolayer graphene in a robust way, keeping them from filling up, so that they can be used for a variety of applications (molecular translocation, water filtering, DNA sequencing, etc). (4) A resolution of a long-standing puzzle about the magnetic properties of epitaxial lanthanum cobalt oxide thin films on different substrates. It was demonstrated that the strain is compensated by ordered oxygen vacancies, which make the films ferromagnetic and insulating, as observed.

Emerging Functionality in Transition-Metal Compounds Driven by Spatial Confinement

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Funding: \$380,000 (2014)

PROGRAM SCOPE

The exotic properties displayed by correlated electronic materials (CEMs) such as the cuprates, manganites, ruthenates, Fe-based pnictides, and heavy-fermion compounds are intimately related to the coexistence of competing nearly degenerate states which couple simultaneously active degrees of freedom—charge, lattice, orbital, and spin states. This project focuses on the exploration of novel behavior induced by spatial confinement, strain, and chemical or physical modification of the surface or interface. Thin films will be grown and characterized *in situ* in an ultra high vacuum environment, using a combination of techniques, such as scanning tunneling microscopy and spectroscopy, low energy electron diffraction, high-resolution X-ray photoemission, angle-resolved photoemission spectroscopy, and low energy electron loss spectroscopy. High resolution scanning transmission electron microscopy, electron loss spectroscopy (BNL), x-ray diffraction, and electrical and magnetic transport measurements will be conducted *ex situ*. We focus on complex doped manganites and ruthenates, exploring the coupled structural, magnetic and electronic transitions. By combining local modifications to order parameters across the range of correlation length scales, we will investigate where the interplay of combinations of spin-charge-orbital-lattice contributions dominate or breakdown. New nanofabrication capabilities at the Center for Nanophase Materials Sciences at ORNL will be utilized to push the size of spatial confinement into the nanometer range. The electronic and magnetic properties can be tuned in

these spatially confined films by depositing electronic donors or acceptors or by patterning of magnetic nano-clusters. Strain also gives a non-thermal parameter to be use to tune electronic or magnetic phase transitions. In essence we are combining two of the grand challenges of the 21st century –Complexity and Nano-structured materials to explore and exploit emergent behavior.

FY 2014 HIGHLIGHTS

An intriguing property of many transition metal oxide thin films is that their physical properties are fundamentally different from what is observed for the bulk. One outstanding example is the nonmetallic behavior in ultrathin films of metallic oxides: a thickness-induced metal-nonmetal transition. We explore the origin of such transition by manipulating thin film growth and combining both macroscopic and microscopic characterization techniques, for $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ (LSMO) ultrathin films. We have isolated several key driving forces -- lattice strain, oxygen vacancies, disorder, chemical segregation and interfacial charge transfer, all of which have noticeable contribution to the metal-nonmetal transition. We find that both tensile and compressive substrate strain increase the critical metal-nonmetal transition thickness. By minimizing strain effect through inserting strained buffer layers, we are able to approach the minimum critical thickness of 4 unit cell (u.c) for the transition. Further capping with a SrTiO_3 overlayer further reduces the critical thickness down to 3 u.c. However, the ferromagnetism of LSMO is more robust against reducing thickness. The ferromagnetic ground state persists down to 2 u.c. films. In particular, with decreasing film thickness, the film exhibits a weak to strong localization crossover behavior with a characteristic onset temperature (T^*) and such crossover is strongly tied with oxygen vacancies. As T^* increases and approaches to the Curie temperature (T_C), the film eventually becomes insulating. Scanning Transmission Electron Microscopy (combining atomically-resolved STEM imaging with electron energy loss spectroscopy) data confirms the surface of the film is terminated with a La/Sr-O layer rather than a MnO_2 -layer. ARXPS results also suggest that Sr segregation tends to be stronger with reduced film thickness, providing new aspects in understanding the metal-nonmetal transition.

Nano-Optical Imaging and Spectroscopy of Correlated Electron Materials

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PROGRAM SCOPE

The combination of optical spectroscopy with scanning probe microscopy has emerged as a new frontier of optical ultra-microscopy with a few nanometer spatial resolution. We have generalized this approach of scattering scanning near-field optical microscopy (s-SNOM) to any optical modality including linear (mid-IR to vis), inelastic (Raman), nonlinear (SHG), and ultrafast spectroscopy, and extended it to variable and cryogenic temperatures. On that basis we have demonstrated a unique application potential for probing nanoscale behavior in correlated, complex, and 2D materials. We pursue the multi-modal and multi-spectral nano-imaging of electronic and vibrational (including Drude and polaronic) resonances, structural symmetry, and ultrafast dynamics to gain insight into properties, mechanisms,

and functions of correlated electron materials (CEM), domain formation in multiferroics, polaronic thermal properties, and finite-size effects, and multivariable and optical control of 2D materials.

FY 2014 HIGHLIGHTS

Combining Drude response s-SNOM with femtosecond pump-probe microscopy we have identified a high degree of heterogeneity controlling the insulator-to-metal transition (IMT) in even single crystals of vanadium dioxide. From studies of the few 10's of femtosecond band structure collapse and nano-domain behavior during the thermally induced phase transition, a high sensitivity to local variations, such as doping, defects, and strain is suggested. This obscures the microscopic mechanism underlying the IMT raising the question on the general role of heterogeneities in correlated electron materials. In studies on graphene, we used phase-resolved surface plasmon interferometry to probe spatial variations of its underlying electronic structure due to edges, defects, and grain boundaries. Charge pooling and local variations in Fermi level, doping, and damping help understand limitations in performance of graphene based devices. Using thermal infrared near-field spectroscopy we investigated phonon-polariton coherence and control associated with the enhanced electromagnetic density of states of phonon polaritons in the thermal near-field. In collaboration with EMSL/PNNL and ALS/LBL we pursue the dissemination of s-SNOM through its implementation at DOE user facilities.

Four-Dimensional Characterization of Dislocation-Defect Interactions in Aggressive Environments - A New Approach

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Funding: \$40,000 (2014)

PROGRAM SCOPE

Electron micrographs provide two-dimensional information of a specific state in time in the evolution of the microstructure. Information in the electron beam direction is missing from the micrograph as is insight to the pathway by which the evolved microstructure developed. This program addresses both issues by advancing the technique of electron tomography of defect structures in metallic systems such that it can be implemented in conjunction with dynamic experimental capabilities in the electron microscope such as straining. The ability to perform experiments in real time with three-dimensional analysis is required to enable advances in mesoscale science. Approaches to minimize the number of micrographs needed to reconstruct the tomogram along with methods to include all defects and the real space coordinate system in the tomogram have enabled quantitative quasi-four-dimensional studies of dislocation interactions with grain boundaries in FCC, BCC and HCP metals as well as dislocation-precipitation interactions in BCC metals. The combination of techniques has provided new insights to the mechanisms of slip transmission across grain boundaries in metals with different crystal structures and the mechanisms by which dislocations bypass large plate-like carbides in body-center cubic systems. Understanding these processes is essential to determining the link between atomic scale processes and macroscale assessment of mechanical properties of pure metals and alloys.

FY 2014 HIGHLIGHTS

The ability to predict the mechanical properties of polycrystalline metals and their alloys depends on determining how dislocations interact with each other and self-organize; how they interact with other obstacles; and how these processes are influenced by external variables such as stress, strain rate, strain and temperature. By combining in-situ TEM straining with electron tomography, the controlling mechanism of slip transmission as a function of temperature has been identified and shown to be the same in face-centered cubic, FCC, and hexagonal close packed, HCP, metals. The magnitude of the Burgers vector of the dislocation left in the grain boundary by the act of transmission determines the slip system activated by the grain boundary to transfer slip. Increasing the deformation temperature enhances the transfer rate but the activated system is still determined by this condition. It has been found that with increasing strain the transfer mechanism can change, the regular boundary structure can be destroyed, and the required change in misorientation across the boundary can generate a discontinuity. It has been found that slip transmission across grain boundaries in body-centered cubic systems appears to involve dislocation emission generally along the boundary. This is in contrast to FCC and HCP metals in which dislocation emission occurs from a specific volume element of the boundary. This dependence of the transmission process on the crystal structure implies differences in dislocation accommodation in the grain boundary as well as the nature of grain boundary dislocation sources. Dynamic studies of the interaction of dislocations with large plate-like carbides in bcc alloys have identified a new mechanism by which the dislocations “feel” the presence of the precipitate and cross slip to avoid interacting with it. The unanticipated finding is that the distance at which cross slip initiates appears greater than the calculated stress field of the precipitate.

Dynamical Nanoscale Electron Crystallography

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PROGRAM SCOPE

This research seeks to employ ultrafast electron crystallography to investigate the complex materials processes of nanoscale correlated oxides and plasmonics-enhanced surface nanoreaction dynamics on metal nanoparticles, with atomistic spatial and temporal resolutions. These efforts build on recent successful ultrafast electron diffraction investigations of vanadium dioxide nanobeams and the surface supported nanocrystals. The proposed research will further benefit from a recent upgrade of the system that incorporates a higher repetition rate (a factor of ten improvement) and an emerging ultrafast electron microscope with radiofrequency (RF) recompression system to significantly enhanced the probe's brightness (>100 improvement) to reach a very high level of signal level and resolution to elucidate the key mechanisms proposed to investigate here. While rather different in their respective applications, a common theme exists in the two: enhanced functionality is enabled on the nanometer scale where selectivity and strong correlations between multiple degrees of freedom play a central role. In particular, in the research of complex materials as realized by microbeam transition metal oxides (VO₂), we are investigating a novel interface-controlled metal-to-insulator transition, which potentially would permit ultrafast manipulation of the electronic state beyond the phonon timescale; on the other

hand, these states can be sustained for long-term storage by coupling the metal-to-insulator transition with structural phase transition. In the case of plasmonics-enhanced photoreactions, the key reaction coordinates to elucidate are the charge-mediated and thermally mediated channels for enhanced photoreactions. By manipulating the local morphology, we aim to control the field-enhancement and prioritize either local charge-transfer-induced or remote resonance-transfer-mediated reaction channels.

FY 2014 HIGHLIGHTS

(1) Optical control of phase transition in strongly correlated electron crystal without lattice entropy: We applied the fs optical doping and temperature control to map out the phase diagram of VO₂ polycrystalline film. By comparing different critical doses from mid-infrared and far-infrared photons, we show that the absorbed photon density rather than the enthalpy is the unifying figure of merit, and hence provided the first direct evidence demonstrating that the optically induced phase transition is driven by the photodoping effect. (2) Correlation-driven dynamics and optical tuning of CDW states in 1T-TaS₂: We report the first comprehensive studies of optical-doping-induced emergence of quantum phases and metastable states in strongly correlated electronic crystal. We showed that optical doping induced phase diagram mimics those under chemical doping and electrostatic charge carrier tuning. We also identified the subtle features unique to fs optical doping, including the induction of the hidden states which may be thermodynamically unstable under most steady-state approach, demonstrating the capabilities of high-speed non-thermal switching at meso-scales based on correlated crystals. (3) Using a high-brightness electron beam system we demonstrated for the first time ultrafast electron micro-diffraction on a single domain in HOPG at single-shot level sensitivity, and diffractive imaging at the scale of 20nm to image the large near commensurate domain dynamics in 1T-TaS₂. (4) Plasmonic enhancement effect at ice-nanocrystal-semiconductor interface: Photocarrier generation quantum yield was investigated using the ultrafast electron diffraction in reflection geometry. In addition to a single-photon enhancement at near surface plasmon resonance frequency, an enhancement at a high frequency dark mode has been established, demonstrating the unexpected complexity at the nanointerface triggered by surface plasmon resonance excitation.

Study of Energy Transport at the Nanoscale

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Funding: \$450,000 (2014-2016)

PROGRAM SCOPE

The proposal seeks to experimentally investigate radiative and conductive thermal transport as well as heat dissipation (generation) at the nanoscale. In macroscale devices, heat transport via radiation and conduction is well described by the Stefan-Boltzmann law and the Fourier's law, respectively. However, recent studies have highlighted that both these laws fail to adequately describe heat transport at the nanoscale. For example, recent computational studies of nanoscale radiative heat transport have suggested that the radiative heat flux in a one-nanometer sized gap between suitably chosen planar dielectric surfaces could be five orders of magnitude larger than what is predicted by the Stefan-

Boltzmann law! This large deviation arises primarily due to contributions from evanescent waves that decay exponentially on a length scale comparable to their wavelength. Proposed Research and Methodology: Several questions regarding nanoscale heat transport and dissipation remain largely unanswered. Some of the most important questions include: 1) How do the radiative transport properties of nanometer-sized gaps (1 - 10 nm) depend on the dielectric properties of the surfaces? 2) Can radiative heat transport be enhanced by orders of magnitude in the extreme near-field? 3) What are the heat transport characteristics of atomic and molecular junctions? 4) Are quantum limited thermal transport properties realizable at room temperatures in metallic atomic chains? 5) What are the heat dissipation characteristics of atomic and molecular scale junctions? 6) Can Peltier cooling be experimentally realized in molecular junctions? Lack of progress in elucidating these nanoscale transport phenomena is primarily due to the experimental challenges in performing measurements with the desired resolution. In this project, we will systematically answer these questions by leveraging the novel scanning probe picowatt-resolution heat-flow calorimeters that were recently developed in our lab.

FY 2014 HIGHLIGHTS

We have recently leveraged the scanning probe techniques developed in this project to establish temperature differentials across nanoscale gaps of novel three terminal devices. Using these devices we demonstrated electrostatic control of thermoelectric properties in molecular scale junctions. Our results provide a rational approach for potentially achieving high efficiency thermoelectric energy conversion using molecular junctions. These results were reports in Nature Nanotechnology. Y. Kim, W. Jeong, K. Kim, W. Lee, P. Reddy, "Electrostatic Control of Thermoelectricity in Molecular Junctions" Nature Nanotechnology (2014)

Using Interfaces to Create Strongly-Coupled Magnetic-Ferroelectrics via Atomic-Scale Heteroepitaxy

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Jointly funded by "Electron and Scanning Probe Microscopies" and "Synthesis and Processing Science"

PROGRAM SCOPE

Our objective is to create a ferromagnetic ferroelectric that can be deterministically switched between symmetry equivalent states using an electric field. The electric-field switching of a magnetization between 180° symmetry equivalent states has not been demonstrated in any material. The required coupling between ferroelectric and ferromagnetic domains allowing such switching is a missing feature in most multiferroics and is key to advancing the field both scientifically and technologically. Starting at the level of electrons and atoms our goal is to rationally design complex oxide heterostructures and interface-materials with this targeted emergent behavior. Using a combination of symmetry arguments and first-principles calculations to explore the connection between structural distortions and ferroelectricity in the perovskite family of materials, we have predicted electrical control of magnetism in the hexagonal rare earth ferrites. These realizations are created with atomic-layer precision, microscopically interrogated to see if there are competing mechanisms to the intended realization, and

finally their macroscopic properties are measured. Here we will develop the scientific ideas and experimental tools necessary to apply this design paradigm to the creation of multiferroics with unprecedented coupling between ferroelectric and magnetic order parameters.

FY 2014 HIGHLIGHTS

We have studied, both theoretically and experimentally, the properties of metastable hexagonal rare-earth ferrites with the $YMnO_3$ structure. In the hexagonal rare-earth manganites ($RMnO_3$), improper ferroelectricity (trimerization) leads to a network of coupled structural and magnetic vortices that induce domain wall magnetoelectricity and magnetization (M), neither of which, however, occurs in the bulk of these materials. It is relegated to the domain walls. Through a combination of first-principles calculations, group-theoretic techniques, and microscopic spin models, we have shown how the trimerization not only induces a polarization (P), but also a bulk M and bulk magnetoelectric effect. This results in the existence of a bulk linear magnetoelectric vortex structure or a bulk magnetoelectric coupling such that if P reverses so does M. We determined the intrinsic properties of the metastable hexagonal polymorph of $LuFeO_3$. We find that hexagonal $LuFeO_3$ is a canted antiferromagnet with $T_N=147$ K and a saturation magnetization, $M_s=0.018 \mu_B/Fe$. We have combined $LuFe_2O_4$ which is ferrimagnetic below 240 K, although it is not ferroelectric, with hexagonal $LuFeO_3$ that is a robust high-temperature ferroelectric with a closely related structure. The resulting precisely engineered $(LuFeO_3)_n(LuFe_2O_4)_m$ superlattices are strong ferrimagnet-ferroelectrics with the highest-known simultaneous transition temperatures. Using scanning transmission electron microscopy imaging and spectroscopy we have mapped the structure, chemistry, and polarization of these artificial multiferroics. Our results show that the superlattices have a higher ferrimagnetic ordering temperature (T_C) than either of the end members, $LuFe_2O_4$ and $LuFeO_3$, from which they are created. T_C increases to nearly room temperature with simultaneous ferroelectricity, suggesting the tantalizing prospect of the existence of the world's first single-phase room-temperature ferrimagnetic ferroelectric.

Spin-Polarized Scanning Tunneling Microscopy Studies of Nanoscale Magnetic and Spintronic Nitride Systems

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Funding: \$180,000 (2014)

Jointly funded by "Electron and Scanning Probe Microscopies" and "Experimental Condensed Matter Physics"

PROGRAM SCOPE

Taking advantage of electron spins in gallium nitride (a Nobel prize-winning technology) is desirable in order to develop its even greater potential as a spintronic material. This project seeks to investigate spin properties in nitride-based material systems down to ultimately small spatial length scales (such as atomic dimensions), using the advanced technique of spin-polarized scanning tunneling microscopy (SP-STM). Using this method, it is possible to obtain information directly about the polarized and unpolarized spin densities of states at surfaces. We have shown through publications the promising spin properties occurring in nitride systems, such as: manganese, manganese gallium, and iron layers

deposited onto semiconducting gallium nitride; manganese and chromium doped gallium nitride layers; and layers of pure manganese and chromium nitrides. We synthesize ultra-thin films of these systems using molecular beam epitaxy (MBE), allowing us to tailor the spin properties with atomic layer precision. The magnetic/spintronic systems are then explored using both STM and SP-STM in which a magnetically functionalized needle-sharp probe is brought to within just a few atomic diameters away from, and then scanned across, the sample surface. Structural, electronic, and spin magnetic properties can be directly obtained as topographical, electronic conductance, and spin conductance images (dI/dV maps), respectively. Correlations among these interrelated properties are provided as the images are simultaneously acquired pixel by pixel. By manipulating tip and sample magnetization using an applied magnetic field, it is possible to deduce 3-dimensional spin information for complex material structures. Such information is also combined with results from different complimentary experimental techniques, and with theoretical calculations as well, in order to address a wide range of fascinating phenomena related to the growth and properties of these materials.

FY 2014 HIGHLIGHTS

Highlights related to the stated program scope include first of all, our work on manganese gallium ultra-thin films (1-25 nanometers) grown on Ga-polar GaN, which was recently published in Applied Physics Letters. We have shown that for the case of slightly Mn-rich growth conditions that there are predominantly three surface reconstruction patterns occurring, including 1x2, 2x2, and 2x3. The most commonly seen 2x2 corresponds to a manganese rich surface having a 3:1 Mn:Ga ratio, in agreement with theoretical calculations; whereas, the film is overall stoichiometric (having a 1:1 Mn:Ga ratio), indicating that excess Mn tends to segregate to the surface of the growing film. Ongoing work is extending to the gallium-rich side of growth, which will ultimately allow a comprehensive understanding of these important magnetic alloys. Secondly, we highlight our discovery of a novel 6x6-patterned surface structure induced by sub-monolayer iron deposition on the atomically smooth, Ga-polar GaN surface. These highly periodic 6x6 structures decorate the surface step edges. First principles calculations find a Ga dimer model consisting of 2/9 monolayers of iron embedded within 7/3 monolayers of Ga, resulting in a relaxed but distorted structure. These results have been published in Applied Physics Letters. Further extension of this work to the N-polar GaN case has also been carried out, which results in completely different structures forming. A final highlight of our recent work is our publication in Review of Scientific Instruments demonstrating the design and capabilities of our low-temperature SP-STM/MBE facility which also includes pulsed laser deposition. This system enables the growth of a wide variety of spintronic materials and their investigation down to the atomic scale under variable magnetic fields at low temperatures. Initial results on the N-polar GaN surface reveal novel features not previously observed in any room-temperature STM images.

EARLY CAREER: Trimodal Tapping Mode Atomic Force Microscopy: Simultaneous 4D Mapping of Conservative and Dissipative Probe-Sample Interactions of Energy-Relevant Materials

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Funding: \$450,000 (2014-2016)

PROGRAM SCOPE

The goal of this project is to develop a multifrequency atomic force microscopy (AFM) method, with which it will be possible to perform rapid measurements of the conservative and dissipative forces between a sharp probe and a nanoscale sample surface, simultaneously as the sample topography is recorded. The new technique will have four-dimensional capabilities, allowing force measurement as a function of the three spatial coordinates and vertical velocity of the probe. The method will be applied primarily to characterize the deformation-dependent electromechanical response of fuel cell ion exchange membranes under accelerated degradation conditions as a function of temperature, relative humidity, and mechanical strain (this work will be conducted in air environments). Additionally, the method will be extended to liquid environments and applied to study the formation process of solid electrolyte interfaces in lithium ion batteries and their evolution during cell cycling. The project will include both experimental and multi-scale simulation activities.

FY 2014 HIGHLIGHTS

We have developed and commissioned a single-pass, trimodal (3-eigenmode) multifrequency AFM methodology that enables simultaneous topographical imaging, modulation of probe-sample indentation and compositional/nanomechanical mapping of soft samples. Within this method, each vibrational eigenmode of the probe serves as a nearly independent 'control knob' that carries out a different function. The new technique is useful for rapidly visualizing and characterizing the subsurface of materials such as polymer composites and biological structures. By varying the indentation depth, the user is able to gradually reveal buried features and create 3-dimensional images of the subsurface. Additionally, we have carried out a variety of bimodal and trimodal multifrequency AFM studies that provide guidance to the user with regards to selecting optimized conditions for maximizing the image contrast without compromising the accuracy of the results (this is often a delicate trade-off in AFM). These studies have been illustrated and disseminated along with measurements performed on commercial and spin-coated proton exchange films.

Probing Correlated Phenomena in Oxide Structures with Quantitative STEM

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PROGRAM SCOPE

The project seeks to further our understanding of atomic structure in strong electron correlation phenomena in complex oxide materials, and to advance quantitative methods for atomic scale imaging of functional oxide materials and interfaces. The project utilizes advances in quantitative scanning transmission electron microscopy (STEM) techniques and in the synthesis of oxide to heterostructures to establish quantitative relationships between atomic structure and the electrical and magnetic properties of correlated oxide interfaces. Experimental techniques include STEM-based diffraction techniques that allow for mapping of small lattice distortions and changes in the oxygen octahedral tilt patterns, with unit cell spatial resolution, at oxide interfaces. These are correlated with phenomena caused by strong

electron correlation physics that occur in these structures, such metal-insulator transitions and magnetism. Methods for quantitative analysis of STEM image intensities to elucidate local arrangements of point defects and nonstoichiometries are being developed in the project.

FY 2014 HIGHLIGHTS

We showed that quantitative HAADF-STEM can be used to obtain complete three-dimensional information about the location of individual Gd dopant atoms in a thin foil of SrTiO₃ [1]. Information is extracted from a single image, thereby avoiding alignment issues of approaches that require multiple images. We show that uncertainties in the depth positions of individual dopants are less than one unit cell in many cases, and that the method provides fully quantitative information of expectation values and establishes a quantitative criterion for the dopant visibility. The overall dopant concentration measured from atom column intensities agrees quantitatively with electrical measurements. Sufficiently thin TEM foils are key for unambiguous interpretation. We investigated the strongly modified octahedral tilts in RTiO₃/SrTiO₃ (R = Gd or Sm) heterostructures (superlattices and quantum wells), and correlated them with phenomena such as magnetism and metal-insulator transitions. Column displacements are measured using HAADF-STEM [2]. Symmetry-lowering structural distortions, measured by quantifying the Sr-column displacements, are present in the insulating quantum wells, but are either absent or very weak in metallic quantum wells, regardless of whether they are embedded in SmTiO₃ or in GdTiO₃. We showed that SrTiO₃ quantum wells embedded in SmTiO₃ remain metallic down to a single SrO layer thickness. The results provided insights into the roles of orthorhombic distortions and electron correlations in the transition to the insulating state. By combining position-average convergent beam electron diffraction (PACBED) with STEM-HAADF imaging, the R-site displacements and oxygen octahedral tilts are measured independently from each other. [1] J. Hwang, J. Y. Zhang, A. J. D'Alfonso, L. J. Allen, and S. Stemmer, *Phys. Rev. Lett.* 111, 266101 (2013). [2] J. Y. Zhang, C. A. Jackson, R. Chen, S. Raghavan, P. Moetakef, L. Balents, and S. Stemmer, *Phys. Rev. B* 89, 075140 (2014).

Imaging Point Defects with Quantitative STEM

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Funding: \$218,000 (2014)

PROGRAM SCOPE

The goal of this project is to develop methods for characterization of single point defects using quantitative scanning transmission electron microscopy (STEM) imaging. Imaging of high atomic number (Z) substitutional impurities and interstitials has been previously demonstrated; the new challenge is to image low-Z impurities, anti-site defects, and especially vacancies. We are working towards imaging vacancies from the decrease in image intensity they create and from the distortions they impose on the positions of neighboring atoms. Both methods are made possible by our recent development of sub-picometer precision, extremely high signal-to-noise STEM imaging using non-rigid registration of a series of STEM images and by detailed, quantitative comparisons to state-of-the-art image simulations of structures derived from density functional theory. We will apply the methods we develop to problems arising from point defects in complex oxide materials relevant to solid oxide fuel cells, starting with the

prototype material (La,Sr)MnO₃. We will use simulations to guide experiments demonstrating the ability to image cation vacancies and cation vacancy / anion vacancy clusters. We will compare the density and spatial distribution of these vacancies and clusters to the predictions of a thermodynamic point defect model based on density functional theory energies, especially near surfaces and interfaces relevant to fuel cell performance.

FY 2014 HIGHLIGHTS

We have demonstrated reproducible sub-picometer precision in STEM images through non-rigid registration of a series of short acquisition time images of the same sample area. The non-rigid registration procedure corrects the instabilities that otherwise limit STEM imaging, enabling image with extremely high signal to noise ratio (SNR). High SNR enables us to locate the positions of atomic columns in the image less than 1% of spatial resolution of the image and to make detailed, quantitative comparisons of experimental image intensities to simulations. We have used high precision imaging to characterize the lattice distortions on the surface of a Pt nanocatalyst. Distortions at edges and corners of such small particles may play an important role in their catalytic activity. We have used DFT calculations to show that cation vacancies and anion vacancies have large binding energies, >1 eV as nearest-neighbor and next-nearest-neighbor clusters for both A-site and B-site cation vacancies. Since (La,Sr)MnO₃ can support both cation vacancies and anion vacancies simultaneously, bound vacancy clusters are likely to occur. STEM image simulations from DFT-derived structures predict that single La vacancies will be detectable in most samples and that single Mn vacancies will be detectable under favorable conditions. Experiments to test these predictions are underway.

Beneath and Between: Structural, Functional, and Spectroscopic Measurements of Buried Interfaces and Interactions

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Funding:	\$200,000 (2014)

PROGRAM SCOPE

Spectroscopic imaging tools and methods, based on scanning tunneling microscopes (STMs), are being developed to examine buried layers and interfaces with ultrahigh resolution. These new methods will measure molecule-substrate bonds, buried dipoles in molecular layers, and key structural aspects of adsorbed molecules, such as tilt angles. We will develop the ability to locate lateral projections of molecular parts as a means of determining the structures of molecular layers. We are developing the ability to measure the orientation of buried functionality.

FY 2014 HIGHLIGHTS

We have found that we can measure and change the valency of the interactions between bifunctional carboranebithiol/selenol molecules on Au{111}. The STM can be used to measure the number of surface bonds, once calibrated with X-ray photoelectron and infrared spectroscopies. The interconversion between one and two surface bonds can be performed through protonation and deprotonation with

acid-base reactions. We have developed methods, in collaboration with Bertozzi, Gilles, and Osher, for the segmentation of domains of carboranethiols, which form two-dimensional plastic lattices. We have ascertained that proximate domains often have aligned dipoles. Thus, having real-time analysis tools has been critical for testing whether the offset between maxima in topographic, which follows the exposed molecular in this case, and in barrier-height imaging, which measures the largest buried dipoles (due here to the dipole of the cage), are due to artifacts or dipole alignment. We have found alignment both within and between domains. Molecular dynamics simulations are consistent with our results. These segmentation and analysis methods are now being applied elsewhere in our laboratory. We have used the segmentation methods, both total variation and empirical wavelets in the analysis of amyloid-forming peptides. We have accelerated the methods such that analyses now take place in real time (our first such structural analysis took two years!) such that missing information can be collected while the sample is still present. We have now advanced this work to the point where we are able to locate metal ions associated with the peptides, which cannot be done crystallographically, because these ions are not arranged periodically. We have used chemical lift-off lithography to produce metal monolayers. We are studying these monolayers, elucidating their chemistry, electronic, and optical properties as well as their potential as substrates for scanning probe and electron microscopy.

Electron Density Determination, Bonding and Properties of Tetragonal Ferromagnetic Intermetallics

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

The project uses quantitative convergent-beam electron diffraction (QCBED) by transmission electron microscopy (TEM) and density functional theory (DFT) to study the electron density and nature of bonding in transition metal based alloys and intermetallics. The methods developed here focus on the bonding charge distribution as one of the quantum mechanical characteristics central for understanding of properties and validation of DFT calculations. The differences between the QCBED measured or DFT calculated electron density and those based on the independent atom model (IAM) can be visualized electron density difference maps (EDDM) which facilitate elucidating details of interatomic bonding in the transition metal based crystals. Multiple structure and temperature factors are measured simultaneously from high-quality crystal volumes by QCBED with sufficient accuracy and precision for comparison with electron density calculations by DFT. The often anisotropic temperature factors for the different atoms and atom sites in chemically ordered phases can differ significantly from those known for relevant pure element crystals due to bonding effects and thus need to be measured, ideally from the same crystal volumes as the structure factors, to facilitate robust electron density determination. The ferromagnetic ordered intermetallic phases FePd and FePt are selected as model systems for 3d-4d and 3d-5d electron interactions, while the intermetallic phases NiAl and TiAl are used to probe 3d-3p electron interactions. Additionally, pure transition metal elements up to Ta with 5d electrons are studied. This effort advances the state of the art in quantitative TEM experimentation, provides original experimental data uniquely suited for new validation approaches of DFT calculations of d-electron affected transition metals and intermetallics.

FY 2014 HIGHLIGHTS

High quality QCBED experiments and associated EDDM enabled study of details of bonding for FCC, BCC and HCP transition metals, FePd (intermetallic and solid solution), as well as for TiAl with slightly Al-rich composition. FCC metals exhibit well defined delocalized bonding charge in tetrahedral sites, while less directional, more distributed bonding charge attains in BCC EDDM's. Agreement between DFT calculated and QCBED EDDM's degrades as d-electron levels fill in the elements, and for intermetallics as d-d interactions dominate over p-d interactions. Utilizing the LDA+U approach enables inclusion of onsite Coulomb-repulsion effects in DFT calculated EDDM's, which can afford improved agreements with QCBED results [1, 2]. This implies that onsite Coulomb repulsion effects become non-negligible as the d-orbitals fill. The use of easily measured low-order structure factors as an additional experimental metric in validation of DFT calculation offers potential to capture better both total energy related properties and details of the interatomic bonding in system with d-electron orbital contributions. Relative to the CBED results the DFT EDDM for the transition metals showed slightly enhanced bonding related delocalized charge between nearest neighbor atoms [2]. QCBED experiments determined differences in the EDDM for the Al-rich and equiatomic composition intermetallic TiAl. Substitution of excess 2at.% Al on the Ti sites appears to redistribute charge from the tetrahedral sites of the FCC related structure to enhance charge delocalization to octahedral sites. QCBED of the equiatomic composition chemically disordered FCC solid solution Fe-Pd delivered isotropic temperature factors about 60% larger than for the chemically ordered intermetallic FePd which has been rationalized in terms of lattice distortion theory. [1] X. Sang, *et al*, Journal of Chemical Physics (2013) Vol. 138, 084504 [2] X. Sang *et al.*, Microscopy and Microanalysis (2014) 20 (S3) 1822.S

EARLY CAREER: *In Situ* Scanning Force Microscopy Studies of Cross-Coupled Domains and Domain Walls

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Funding: \$150,000 (2014)

PROGRAM SCOPE

The objective of this project is to explore the nanoscale emergent phenomena and to understand the unconventional properties of cross-coupled domains and domain walls in multiferroics, where both ferroelectricity and magnetism coexist. The giant magnetoelectric effect due to coupled ferroic orders in multiferroics is of both fundamental and technological interest and is promising for energy-efficient multifunctional applications. The presence of domains and domain walls is a distinguishing feature of any ferroic order; their responses to external stimuli determine the macroscopic properties and the functionalities of ferroic materials. To address the challenges and to directly visualize the cross-coupled domains and domain walls and their responses to the applied electric and magnetic fields, this project will develop a unique, high-resolution and high-sensitivity *in situ* scanning force microscopy (SFM). The real space imaging of domains and domain walls by SFM aims to fundamentally understand the nature of magnetoelectric cross-coupling in representative multiferroic and magnetoelectric materials.

FY 2014 HIGHLIGHTS

We developed a novel Magnetoelectric Force Microscopy (MeFM) technique that combines Magnetic Force Microscopy with in-situ modulation of high electric fields. This microscopy technique enables direct visualization of the magnetoelectric response of the domains in multiferroic materials (e.g., hexagonal manganites). The interesting observation of the sign change of magnetoelectric response at each structural domain wall was explained by theorists at Cornell and Groningen (Netherlands) using symmetry analysis and phenomenological modeling, which provides compelling evidence that the magnetoelectric coupling is mediated by a periodic lattice distortion. Furthermore, the MeFM results revealed a gigantic enhancement of magnetoelectric effect when the magnetic order can rotate freely, suggesting a viable way to enhance magnetoelectric couplings for potential multifunctional applications. The detection of magnetoelectric response at mesoscopic scales not only allows direct visualization of magnetoelectric domains, but also opens up explorations of exciting emergent phenomena in multifunctional materials with multiple coupled orders. In addition to MeFM, we developed a Background-Free Piezo-response Force Microscopy (PFM), which effectively removes the “system inherent” background, allowing high sensitivity PFM measurements of new dielectric materials such as multiferroics and improper ferroelectrics.

Transport and Imaging of Mesoscopic Phenomena in Single and Few Layer Graphene

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Funding: \$400,000 (2014)

PROGRAM SCOPE

The research objective of this project is to investigate novel quantum phenomena in single and few layer graphene. Special emphasis is given to the role of Coulomb interactions and to spatially varying phenomena where geometry and boundary conditions play an important role. Our experimental approach consists of both conventional transport methods as well as sophisticated local probe techniques capable of imaging the local thermodynamic and transport properties of these spatially varying quantum phenomena. We explore both naturally occurring inhomogeneities due to intrinsic disorder as well as spatially dependent phenomena arising from patterning graphene into nanostructures, introducing inhomogeneous charge densities or magnetic fields using local electrostatic gates, superconducting contacts, and contacting graphene with novel materials. Our focus is on extremely high quality few layer graphene fabricated either by suspending above a substrate or using h-BN as a support structure. Such devices have very small disorder where mesoscopic and relativistic-like phenomena in the ultra-low density regime may be studied. A few examples include the investigation of the fractional quantum Hall effect and the effects of screening on such correlated phenomena, and the investigation of hybrid superconductor-graphene devices.

FY 2014 HIGHLIGHTS

(1) We have observed an anomalous fractional quantum Hall (FQH) effect in bilayer graphene. Our measurements use a scanning single electron transistor to image the local compressibility of bilayer

graphene on h-BN. The observed sequence of FQH states and the background inverse compressibility pattern break particle-hole symmetry and instead follow a $\nu \rightarrow \nu + 2$ pattern. The $\nu \rightarrow \nu + 2$ symmetry that we observe indicates that the orbital degeneracy uniquely present in bilayer graphene is playing an important role. (2) We have induced a quantum spin Hall (QSH) state in monolayer graphene by subjecting a high quality graphene sample to a large magnetic field angled with respect to the graphene plane. Unlike previous realizations of QSH states observed in HgTe and InAs/GaSb quantum wells, this graphene QSH state is fundamentally built upon the graphene quantum Hall effect and the effects of electron-electron interactions. This approach is inspired by the similarity between the quantum spin Hall state and overlapping electron and hole-like copies of the quantum Hall effect, with the two copies having opposite spin polarizations. We have demonstrated that such a state can be induced in graphene by inverting its electron- and hole-like Landau levels through the effect of Zeeman splitting, which is induced by a large in-plane magnetic field and exchange interactions.

Probing Correlated Superconductors and their Phase Transitions on the Nanometer Scale

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Funding: \$240,000 (2014)

PROGRAM SCOPE

Our experimental program provides an atomic scale perspective of unconventional superconductivity – how it evolves from an unconventional conducting state, and how it competes with other forms of order in correlated electronic systems. Such phenomena are at the heart of some of the most debated issues in condensed matter physics, and their understanding is an intellectual driver for many of the DOE-BES projects for the development of novel materials, including the search for higher temperature superconductivity. Our aim is to provide a microscopic view of these exotic materials and their phase transition into the superconducting state using some of the most sophisticated scanning tunneling microscopy (STM) and spectroscopy techniques. The results of the experiments proposed here provide important evidence that will help constrain theoretical models of unconventional superconductivity, the normal states from which it emerges from, and electronic states with which it competes. The proposed program is divided into three parts. The first part will focus on examining how heavy electron states emerge in compounds in which the f orbital interacts with more itinerate electronic states and the process by which such heavy electronic states give rise to unconventional superconductivity. The second part of the proposed program will focus on how charge ordering competes with superconductivity in high- T_c cuprates. One of the key questions is to determine whether there is universality in the way charge ordering occurs in doped Mott insulators and the connection between different forms of charge ordering now observed in different cuprate families. The third, and more exploratory part of this program, will focus on the development of techniques for local Josephson tunneling with superconducting STM tips at millikelvin temperatures.

FY 2014 HIGHLIGHTS

Science 343, 393 (2014). For each of the past several years, our group has accomplished a major breakthrough in understanding the properties of high- T_c cuprate superconductors. This past year, our

group demonstrated the major experimental results showing the ubiquity of charge ordering in cuprates and its competition with superconductivity. To put this work in context, we should first note that in 2004 (M. Vershinin *et al.*, Science 2004), our group established the observation of a charge ordering signal in the temperature range above T_c in underdoped Bi-based cuprates. In the interim years, we went on to establish that this signal could be detected at the onset of the pseudogap state at T^* as well as it having the strongest signal near 1/8 doping, similar to the stripe phase in La-based cuprates found in late 1990s. In a recent combined study of charge ordering using both high-resolution, temperature-dependent spectroscopic mapping with the STM, as well as resonant elastic x-ray scattering (REXS) on the same sample, we have made several important contributions. First, we have established that the charge ordering seen with the STM is present at the same wavevector in the REXS measurements. Depending on the doping, we find this wavevector to be the same as that of Y-based cuprates or La-based cuprates, thereby establishing universality of a charge ordering mechanism across all families of cuprates. Second, we find that both the STM and REXS signals confirm that the charge ordering competes with superconductivity as it becomes weaker with decreasing temperature below T_c , where superconductivity gets stronger. Third, using the energy resolution of the STM together with its ability to obtain information about the momentum of the quasiparticles by using their interference, we established a connection between the end of the arcs of a pseudogap in momentum space and the charge ordering wavevector.

Electron Nanocrystallography of Complex Materials and Processes

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Funding: \$460,000 (2014-2016)

PROGRAM SCOPE

The project is to develop a quantitative and spatially-resolved characterization approach that will enable the study of evolution of polarization domains and symmetry in complex piezoelectric crystals. A new and quantitative method for the determination of local polarization and crystal symmetry will be developed and validated, and the method will be applied together with in-situ experiments to the study of relaxor-ferroelectric crystals. Polarization determination is based on the measurement of local structure factors by recording a large number of convergent beam electron diffraction (CBED) patterns using a scanning electron nanoprobe. To achieve this, an advanced automated refinement procedure will be developed using electron multiple scattering theory. It is anticipated that through the proposed new approach, critical data will be obtained about polarization rotation and domain wall dynamics and their correlation with external forces. The outcome of the research will make it possible to predict quantitatively domain evolutions under force and to shed new light on the mechanisms of high performance piezoelectric crystals. The local structure factor measurement method developed here is also general; applications of this method will have significant impacts on the study of local structures, especially in highly doped materials. The experiment will be carried out using advanced imaging and diffraction techniques, such as a direct electron detection camera to reduce the electron dose in order to minimize the electron beam effect on polarization switching, to enable fast diffraction pattern acquisition rate up to 1600 frames per second for time dependent study. In-column energy filter will be

employed for quantitative CBED. The in-situ experiments will be helped by a Hysitron PI95 TEM Picoindenter.

FY 2014 HIGHLIGHTS

(1) Symmetry determined in ferroelectric single crystals of PMN-PT: By quantifying the symmetry recorded in the experimental CBED patterns, we show that the symmetry of PMN-31%PT is triclinic at few nm length scales, and becomes monoclinic (MB)-like symmetry at the length scale of few tens of nm. The macroscopic symmetry determined by X-ray diffraction suggests multiple domains of different sizes in PMN-31%PT single crystal. Thus, the high piezoelectric response of PMN-31%PT single crystal at the morphological phase boundary (MPB) region is underlined by the structure that lacks local symmetry, which has an averaged monoclinic symmetry over tens of nanometers in some regions of the crystal. By comparing the experimental and the calculation results, therefore, the lack of local symmetry observed in the experimental CBED patterns is not a result from the R- and T-nanodomain structures but a result from an intrinsic structural property of PMN-31%PT single crystal. (2) Fluctuations in local symmetry revealed by CBED: Direct evidence for the volume dependence and spatial dependence of symmetry fluctuations was obtained in PMN-31%PT by CBED with help of energy dispersive x-ray (EDX) spectroscopy. Fluctuations in symmetry were determined by using different electron beam probe sizes ranging from ~2 to 25 nm from a crystal ~62 nm thick. The symmetry of PMN-31%PT was found to increase linearly as the average volume increased, and the local symmetry fluctuated from one location to another at the nanoscale. The EDX spectroscopy results indicate chemical fluctuations are significant only when the probe size decreases to ~2nm. We attributed the symmetry fluctuation to locally varying composition, composition dependent ionic displacements, and spontaneous polarization.

DOE National Laboratories

Soft Matter Electron Microscopy Program

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Students: 2 Postdoctoral Fellow(s), 4 Graduate(s), 0 Undergraduate(s)
Funding: \$969,000 (2014)

PROGRAM SCOPE

Our objective is to reshape the way microscopy and scattering techniques are used to investigate structure, composition and transport properties of soft matter used in emerging clean energy-related applications including lithium batteries and hydrogen fuel cells. We will study a wide array of materials ranging from sequence-specified bio-inspired polypeptoids to synthetic block copolymers made by anionic polymerization. The proposed electron microscopy work focuses on determining the morphology of ion-containing nanostructures, maximizing spatial and energetic resolution while minimizing radiation exposure and damage. This will be achieved by using novel techniques to

manipulate and detect the incident, transmitted, and scattered electrons. We pay particular attention to determination of both the 'average' morphology and statistical fluctuations around the average; fluctuations are an essential property of soft matter. We will combine hard X-ray and electron tomography to obtain high-resolution images of dendritic structures that are the root cause of failure of batteries with lithium metal anodes. This combination of techniques is needed because the dendritic structure is an isolated object, like the proverbial 'needle in a haystack'. Energy-resolved soft X-ray scattering will be used to determine the local chemical environments around the ions. The relationship between molecular structure, morphology, and ion transport on the mesoscale will be clarified by the use of polymer chains with precisely specified sequences and through the use of molecular simulations with validation through simulated characterization. Included in this effort is the first theoretical attempt to quantify observed shifts in low loss electron energy loss spectra from first principles.

FY 2014 HIGHLIGHTS

We have produced the first electron micrographs demonstrating the presence of pure water channels in hydrated fuel cell membranes. An important barrier in enabling hydrogen fuel cells is the availability of a suitable electrolyte membrane for proton transport between the electrodes. Designing ideal membranes, however, requires a fundamental understanding of the mechanism of proton transport in the membranes which requires the development of new characterization tools. The importance of water-rich channels for proton transport is well-established but little is known about the structure of these channels. We obtained high resolution images of these channels in the model polymer electrolyte membrane. Equilibration of the membrane in humid air resulted in homogeneous water-rich channels. In contrast, equilibration of the membrane in liquid water resulted in the formation of a heterogeneous proton-conducting channel comprising a central layer of pure water enveloped within polyelectrolyte brushes. The formation of the pure water layer coincided with a significant increase in proton conductivity. In fact, the estimated conductivity within the layer was comparable to that of an equivalent hydrochloric acid solution. Filtering of the raw electron micrographs within certain spatial frequencies, and our use of model block copolymers with well-defined periodic morphologies were essential for determining the presence of water-rich channels.

Probing Phase Transitions, Chem. Reactions, and Energy Transfer at the Atomic Scale: Multifunctional Imaging with Combined Electron and Scanning Probe Microscopy

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Funding: \$721,000 (2014)

PROGRAM SCOPE

The focus of the program is on probing the mechanisms of reversible and irreversible bias-induced transformations in solids at the atomic level of individual defects using a combination of scanning transmission electron microscopy (STEM) and local-field confinement in ex-situ and in-situ active device configurations. We aim to unravel the complex interplay between order parameter dynamics, ionic flows, electrochemical reactions, and mechanical behavior by studying three classes of phenomena: (a)

irreversible electrochemical processes including oxygen vacancy injection and vacancy ordering; (b) hysteretic processes including electrostatically-driven structural changes and phase transitions in ferroelectrics and at ferroelectric interfaces; and ultimately (c) kinetics of reversible electronic transfer, ionic polarization and interfacial reactions at oxide interfaces and oxide grain boundaries. We aim to uncover the mechanisms of these transformations at the nanometer-scale, and ultimately, the single-atom and single electron level, and link these to atomistic and mesoscopic models. The experimental and quantification approaches are developed for *ex situ* experiments, in particular systems with built-in electric fields or compositional gradients. They are subsequently used in *in situ* studies, where types of information inaccessible by other techniques can be obtained, such as direct images of metastable states and real-time compositional snapshots. The transformation mechanisms uncovered in this project will help establish a sound scientific basis for optimization and engineering of materials for a broad range of energy and information technologies from solid oxide fuel cells to memristive data storage and logic devices, as well as elucidate the role of vacancies in physical functionality of surfaces and interfaces.

FY 2014 HIGHLIGHTS

(1) DOE highlights submitted: “Direct observation of ferroelectric field effect and oxygen vacancy screening at ferroelectric-metal interface” (Aug. 2014); “Polar behavior induced by oxygen vacancy ordering” (May 2014). (2) Investigated unexpected polar behavior in $\text{LaFeO}_3/\text{SrFeO}_3$ superlattices made of two non-polar oxides, concluding that it is driven by the ordered oxygen vacancies. (3) Investigated surface-related effects in BiFeO_3 thin film, from the small reconstructed layer to domain wall widening on approach to the interface, directly determining a spectrum of length scales for different surface phenomena. (4) Developed image quantification approaches suitable for rapid analysis of multiple images and used it to investigate quantitative aspects of vacancy dynamics in $\text{LaCoO}_3/\text{SrTiO}_3$ multilayers, enabling tracking of the composition of each individual unit cell as the system converges to a vacancy ordered state. (5) Investigated vacancy distribution and interface structure in $(\text{La,Sr})\text{CuO}_2$ superconductors grown on different substrates and concluded that different levels of strain can lead films to adopt different oxygen stoichiometry, in turn affecting superconducting properties. (6) U.S. Patent No. 8,752,211, issued: June 10, 2014 “Real Space Mapping of Oxygen Vacancy Diffusion and Electrochemical Transformations by Hysteretic Current Reversal Curve Measurements”.

Fundamental Mechanisms of Transient States in Materials Quantified by Dynamic TEM

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Funding: \$971,000 (2014)

PROGRAM SCOPE

The goal of this project is to investigate the fundamental physical mechanisms controlling transformation kinetics at the nanoscale, concentrating on the crystallization of amorphous solids. These kinetics are influenced by the initial amorphous structure, which can be controlled by processing. We

will use fluctuation electron microscopy (FEM) to characterize the structure of several model amorphous systems, including Ge, Si, and phase change materials, which have been formed under different conditions. We will use atomistic simulations to create structures that we will use to simulate the FEM signals to get a best match and then measure crystallization kinetics with those various structures in the simulations. We will then perform precise measurements of crystallization nucleation rates and growth rates in those films, which are enabled by the unique capabilities of the dynamic transmission electron microscope (DTEM). We will use phase field simulations at the mesoscale to connect the thermodynamic quantities from atomistic scale simulations to the microscopic observations from the DTEM. We will then compare the observed differences in the kinetics with the predictions of simulations to reveal fundamental controlling mechanisms for the transformation process.

FY 2014 HIGHLIGHTS

Conducted experiments on pulsed-laser dewetting in Co-Cu alloys to investigate the self-assembly of nanoparticle arrays on substrates. This work is in collaboration with Prof. Philip Rack at the University of Tennessee and makes use of the Center for Nanophase Materials Sciences, sponsored by BES at Oak Ridge National Laboratory. Performed movie-mode DTEM experiments to study rapid crystallization of amorphous Ge, measuring growth kinetics in the three different regimes of crystallization. We have also performed preliminary fluctuation electron microscopy experiments, which showed a distinct change in the medium-range order in amorphous Ge caused by sub-threshold laser annealing. Performed movie-mode DTEM experiments to study rapid crystallization of amorphous GeTe, thin film instabilities in GeTe, and unsteady propagation in reactive multilayer metal foils. Developed a phase-field model and a corresponding computer code for simulating microstructure evolution during a reactive phase transformation involving intermixing of layers and crystalline-amorphous-B2 structural transition in Al/Ni multilayers. Parameterized the phase-field model with thermodynamic and kinetic parameters computed by the classical molecular dynamics method. Conducted preliminary phase-field simulations to investigate the fundamental kinetics of interphase boundary evolution.

STEM: Atomic Structure and Properties of Materials

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Beth Guiton; Kentucky, University of
Students: 4 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding: \$2,508,000 (2014)

PROGRAM SCOPE

The mission of the STEM group is to develop instrumentation and techniques to advance atomic level characterization and to use these to explore the behavior of materials at the atomic scale. The successful correction of aberrations in our Nion UltraSTEM 200 scanning transmission electron

microscope now provides 0.57Å resolution imaging, combined with unprecedented sensitivity for spectroscopy. This instrument's resolution even at 200 kV is now limited by chromatic aberrations. With this tool, the group probes the connections between a material's spin, charge, orbital and structural degrees of freedom. This project primarily investigates critical issues in selected model materials systems; defect configurations in two-dimensional materials, complex oxide heterostructures, and materials for energy applications. Density functional theory is used to interpret the data and make the connections between the microscopic and macroscopic properties that are of interest for potential applications.

FY 2014 HIGHLIGHTS

The STEM group created, activated, observed and explained the ultimate miniaturization of a mechanical device (a terahertz rotor). This result obtained with theorists at Vanderbilt University (Lee and Pantelides), was published in *Angewandte Chemie*. The same team also demonstrated the existence of stable holes in graphene. This discovery is a major step toward the development of nanopore devices that could be used, for example, for DNA sequencing. In several papers published in high impact factor journals, the STEM group and collaborators have described novel charge and magnetic properties that develop at complex oxide interfaces. These include a charge profile tunable by strain, chemical doping or electron-lattice interactions and the development of interfacial ferromagnetic coupling that can be controlled by a voltage. We have quantitatively mapped dopant distributions and tracked dopant diffusion in three dimensions with single atom sensitivity. These achievements obtained from Se-doped MoS₂ and Ce- and Mn-doped AlN have been published in *Nano Lett.* and *Science Rep.* The group published 37 refereed journal articles and 5 refereed conference proceedings; Six of these were published in *Nature* journals and three in *PRL*. Maria Varela was awarded the Burton Medal for distinguished contributions to the field of electron microscopy. Matthew Chisholm was awarded a patent for band gap tuning in transition metal oxides.

Spectroscopic Imaging STM for Complex Electronic Matter Studies

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Funding: \$620,000 (2014)

PROGRAM SCOPE

Everything around us, everything each of us has ever experienced, and virtually everything underpinning our technological society and economy is governed by quantum mechanics. Yet this most fundamental physical theory of nature often feels as if it is a set of somewhat eerie and counterintuitive ideas of no direct relevance to our lives. Why is this? One reason is that we cannot perceive the strangeness (and beauty) of the quantum mechanical phenomena all around us by using our own senses. In this program we develop techniques that allow us to image complex quantum electronic matter directly at the atomic scale. For example we visually explore the previously unseen and very beautiful forms of quantum matter making up electronic liquid crystals; hybridized heavy-fermions; topological-insulator surface states; and topological superconductors. We explore implications for fundamental research, and also for

advanced materials and new technologies, arising from the development and application of these novel techniques.

FY 2014 HIGHLIGHTS

(1) Imaging of Dirac-Mass Configurations in Ferromagnetic Topological Insulators: We recently introduced the Dirac-mass 'gapmap' technique to visualize the atomic-scale spatial conformations of Dirac mass. It reveals radically new perspectives on ferromagnetic topological insulators. We discover intense nanoscale disorder in the Dirac-mass and demonstrate that this is directly related to the magnetic-dopant atom density $n(r)$. This reveals how the percolating internal edge states at the $\Delta(r)$ domain walls can destroy all exotic topological insulator (TI) surface state phenomena. (2) Gap Structure of Topological Superconductor Sr_2RuO_4 : To establish the mechanism of topological superconductivity in Sr_2RuO_4 , a necessity is knowledge of the momentum-space structure of the energy gaps. Our measurements of the density of states in superconducting Sr_2RuO_4 for T between $0.1T_c$ and T_c demonstrate that the maximum value $2\Delta \sim 5kT_c$, plus our discovery of a $N(E)$ shape indicative of line nodes, are consistent with magnetically mediated quasi-one-dimensional superconductivity on two specific bands. (3) Visualization of Heavy Fermion Superconductivity: Cooper pairing of heavy-fermions was hypothesized as due to spin-fluctuation exchange but was impossible to prove because energy scales for both band and gap structures are so low (sub meV). To solve this challenge, we introduced Bogoliubov quasiparticle interference (QPI) imaging using millikelvin STM in CeCoIn_5 and revealed both the heavy-fermion band structure and superconducting $\Delta(k)$ of a heavy fermion compound for the first time. (4) Proof of Cooper Pairing Mediated by Magnetic f-Electrons in CeCoIn_5 : We invented a technique to measure the f-electron magnetic interactions of CeCoIn_5 . Solving the superconducting gap equations with these magnetic interactions mediate the Cooper pairing, we made quantitative theoretical predictions. We established agreement between these and measured characteristics of CeCoIn_5 indicating magnetically mediated pairing.

EARLY CAREER: Investigation of the role of inhomogeneities and phase segregation on correlated electron dynamics by optical spectroscopy and nano-imaging

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Students: 0 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding: \$2,500,000 (2010-2014)

PROGRAM SCOPE

The purpose of this project was twofold: a) to develop novel instrumentation which enables performing infrared optical spectroscopy measurements with nano-scale spatial resolution within a variable temperature environment. b) to use this tool either in order to address physics problems which are difficult/impossible by other type of instrumentation or for providing a complementary perspective in conjunction with other established techniques. Scanning Near Field Optical Microscopy (SNOM) has several key features among which: nano-scale spatial resolution; chemical sensitivity reaching the single molecule level, compatibility to time resolved methods; opportunity for finite-momentum optics. Our instrumentation goal was to add to this list SNOM operation in a 10 K – 300 K temperature range. These key advantages were aimed at studying competing phases in correlated systems (e.g. phase transitions,

the role of intrinsic/extrinsic inhomogeneities) and emergent phenomena associated with surfaces or buried interfaces in artificial structures. Our current work is focused on three main projects: 1) Electronic properties of graphene: Here we are interested in the origin of damping in a quasi-2D electronic gas with relevance for graphene-based electronics. We use near-field plasmon interferometry which allows us to extract temperature dependent energy-momentum information about collective electronic excitations. 2) Metal-Insulator transition and ferromagnetism in thin sub-surface EuO films. Can the metal-insulator (M-I) transition in thin subsurface EuO be detected optically by SNOM? Does the giant magneto-resistance exhibited by EuO belong to the paradigm of manganites? Can we offer insights for a roadmap to spintronics application? 3) High-temperature superconductivity. Here we exploit the capability of SNOM to image superfluid-polaritons in the superconducting states. We want to understand how can one use interface physics to further increase the maximum T_c in superconductors?

FY 2014 HIGHLIGHTS

The key project finalized during the last year is the successful and reproducible operation of our infrared cryo-SNOM at both room and low temperatures*. Other results: (1) Electronic properties of graphene. We performed real-space mapping of plasmon scattering in a single-layer of commercial graphene. We observed heavily damped plasmonic waves indicative of remarkable scattering efficiency of folds or sub-nanometer cracks. Discriminating between intrinsic and extrinsic damping mechanisms via temperature dependent studies requires a gated device: particle desorption in vacuum leads to drastic changes in the Fermi levels. We use ultra-high mobility samples consisting of single-layer graphene (SLG) sandwiched between boron nitride layers (ongoing collaboration with Philip Kim's group, Columbia/Harvard University). (2) Studies of thin EuO films. We studied 18 nm EuO thick films protected by a 23 nm a-Si. We found that the signal measured at $T > T_c = 69$ K is about 50% lower in intensity than below T_c and that the sample is optically homogeneous sample above and below T_c . Our results indicate that SNOM can probe the subsurface M-I transition in EuO and that the giant magneto-resistance is not related to inhomogeneous behavior. Our next set of measurements will be quantitative and will consist of SNOM data of EuO with in-situ Au reference as well as magnetic force microscopy (MFM) measurements (work in progress, collaboration with Darrell Schlom's group, Cornell University). (3) High- T_c superconductivity. We are just about to demonstrate cryo-SNOM operation in the 0.1 – 1 THz range. We acquired all equipment needed for these measurements and we were successful in producing and testing at all temperatures our AFM probes compatible with this operation: 65 kHz quartz tuning forks with W and Au etched wires (shaft lengths ≥ 500 μm).

Probing Coupled Metal-Insulator and Ferroic Transitions from the Atomistic to Mesoscopic Scales

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Funding: \$775,000 (2014)

PROGRAM SCOPE

The coupling between electronic and ferroic behaviors has emerged as one of the most intriguing aspects of condensed matter physics, with examples including phase separation, metal-insulator transitions, and complex electronic ordering patterns. Both structural and electronic aspects of these

behaviors are currently of interest for energy generation and storage applications. The overarching goal of this project is to reveal the mechanisms of coupled electronic (metal-insulator) and ferroic (ferro- and antiferroelastic, ferro and antiferroelectric) transitions from atomistic to mesoscopic scales by exploring coupled electronic and atomistic structures on the length-scale of an individual unit cell, single domain, structural defect, and domain wall. The research will develop and exploit the synergy between advanced scanning probe microscopy, artificial-intelligence and multivariate methods for theory-experiment matching, and established methodologies of surface science and oxide growth. The SPM tip will act as a local probe of the ferroic and electronic state of matter, communicating local properties to the outside world through imaged structure and measured electronic current, dynamic and static electromechanical response, resonant frequency and quality factor of the cantilever, and microwave response, thus exploring and actively manipulating local order parameters in nanoscale volumes. Unraveling and subsequently understanding the energy balance between competing interactions and establishing the atomic configurations responsible for desired materials functionalities will reveal the key structural and electronic mechanisms involved in energy storage, generation and dissipation processes. This will provide a fundamental scientific basis for optimization and engineering of energy-related materials, with enormous potential benefits to fuel cells, batteries, solar energy, data storage, energy transport, and other vital energy technologies.

FY 2014 HIGHLIGHTS

In the concurrence period, we explored the coupled physical and chemical phenomena on the $\text{La}_{(0.625)}\text{Ca}_{(0.375)}\text{MnO}_3$ (LCMO). We identified preferred surface reconstruction during growth and demonstrated the influence of oxygen pressure and epitaxial strain on Mn adatom mobility and atomic-scale surface morphology of manganite thin films using atomically-resolved scanning tunneling microscopy and in-situ diffraction and spectroscopy methods. We further developed pathway to control surface reconstructions caused by oxygen vacancy ordering via silver-doping. Finally, we demonstrated feasibility of electrochemical single-atom manipulation on in-situ grown surface. To enable further progress, we developed a novel, big-data approach to analysis of reflection high energy electron diffraction (RHEED) data during epitaxial growth. The approach facilitates control over surface morphology, and in conjunction with in-situ STM will allow growth of films with controlled surface structures. In parallel, we explored emergence of ferroelectric domain structure and ferroelectric size-effect in an intrinsically layered ferroelectric material, CuInP_2S_6 as a model for atomically resolved studies of ferroic ordering. On the mesoscopic level, we demonstrated deterministic control over polarization orientation in-plane at any angle, by decoupling ferroelectric order parameter from crystallography on mesoscopic scale and thereby greatly increasing theoretical attainable densities for ferroelectric memory storage devices. We further performed disorder mapping and uncovered universal relaxation processes on surface of a relaxor ferroelectric through synergistic combination of multidimensional scanning probe techniques and multivariate statistical analysis.

Nanometer-Scale Surface and Interface Phenomena

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Students: 2 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding: \$615,000 (2014)

PROGRAM SCOPE

The four tasks of this program study solid surfaces, internal interfaces and solid-liquid interfaces. The overarching goal is to achieve a fundamental understanding of the processes that control the static and dynamic properties of surfaces and interfaces and use this knowledge to provide the foundations for new energy technologies consistent with DOE's Office of Basic Energy Sciences mission. To achieve this goal, we apply a wide range of state-of-the-art experimental and tools and theoretical approaches to determine how atomic-scale processes relate to the longer-range interactions that control interfacial behavior. Specific materials systems are chosen for their relevance to national needs, notably energy-related materials. Our task structure is designed to investigate a set of increasingly reactive environments from clean surfaces in ultrahigh vacuum, to liquid-solid interfaces, to metallic and oxide nanostructures in electrochemical environments: Task 1 focuses on atomistic processes on surfaces; Task 2 describes the collective behavior that occurs on larger length scales; Task 3 deals with linking the results of Tasks 1 and 2 to macroscopic properties of technological importance; and finally Task 4 is concerned with explaining electrochemical processes in terms of nanoscale interfacial properties.

FY 2014 HIGHLIGHTS

- Characterized the structure of single-layer tungsten diselenide with low energy electron microscopy.
- Determined that surface oxygen is crucial to growing perfect graphene crystals on copper.
- Used low energy electron microscopy to show that 2-D boron nitride grows epitaxially next to graphene.
- Characterized the growth modes of various iron oxides on ruthenium surfaces.
- Determined how graphene grows on palladium.
- Explained how surface nucleation barriers determine the charging rates of batteries with LiFePO₄ battery electrodes.
- Successfully modeled experiments of Au diffusing into bismuth telluride.
- Showed that binding of graphene edges to the substrate determined the shape of growing graphene crystals.
- Explained at an atomic scale how magnetite converts to hematite in an oxygen rich environment.
- Made first real-time observation of graphene changing orientation while bonded to a substrate.
- Determined and modeled the structure of the surface of magnetite at high temperatures.
- Used low energy electron microscopy to probe the amount of disorder in bilayer graphene.

3D Visualization of Emergent Behavior in Nanoscale Functional Heterostructures

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Funding: \$969,000 (2014)

PROGRAM SCOPE

The properties of ferroic materials at the nanoscale are governed by their complex energy landscape, which must be understood if emergent behavior is to be controlled. Our goal is to gain a fundamental understanding of how the energy landscape can be influenced through geometric patterning or confinement and through interfacial interactions. We are focusing our research on heterostructure nanosystems whose building blocks show ferromagnetic, ferroelectric, and resistance switching properties. We aim to obtain a fundamental understanding of domain behavior and charge transport properties in these nanostructures through control of parameters that contribute to their energy landscape, such as interlayer coupling, geometric effects, and interactions between adjacent nanostructures. As the nanostructure dimensions approach the characteristic length scales of the order parameters and associated energy terms, novel distributions of spin and/or charge are created. Further degrees of freedom can be achieved in 'designer' heterostructures, in which there is coupling between the order parameters in materials with different ferroic order. Our approach involves an interwoven combination of aberration-corrected Lorentz transmission electron microscopy and advanced scanning probe microscopy that we use to address scientific questions related to ferroic nanostructure behavior, for example the competing effects of exchange-bias and interlayer exchange coupling in ferromagnetic nanostructures or the role of metastable ferroelectric domains on polarization switching in thin films. A particular focus is the use of three-dimensional analysis and imaging techniques that we have developed to visualize domain and transport behavior in nanostructures as a function of external stimuli such as applied fields, temperature and/or time.

FY 2014 HIGHLIGHTS

(1) We carried out the first observation of a volatile photovoltaic-like resistance change in Pt/TiO₂/Pt heterostructures induced by exposure to a synchrotron X-ray beam. A non-volatile effect was also observed, resulting from X-ray-induced defect generation and Joule heating, that led to the formation of conducting Ti₄O₇ channels. (2) We used Lorentz TEM and quantitative phase reconstruction to explore the energy landscape of Co nanospirals and determined that the shape anisotropy controlled the spin structure leading to uniform magnetization along the spiral. (3) We have developed a new technique - Charge Gradient Microscopy (CGM) – that can be used to reveal the underlying polarization domain structure in ferroelectric materials at high speeds by scraping off and quantifying the surface screening charge. We envision that CGM can be used to study the complex dynamics of domain nucleation and growth in different environments. (4) We investigated the origins of resistance changes in Pt/CuO_x/Pt nanostructures and correlated them with local changes in copper oxidation state, using x-ray nanoprobe spectro-microscopy and current-voltage characterization. (5) We developed a theoretical model to analyze the effect of shape on the ferroelectric polarization of nanoparticles in the absence of screening charges. Using this model, we determined the minimum aspect ratio of a triaxial allipsoid that can sustain ferroelectric polarization and visualized using phase retrieval methods in TEM.

Spin Physics

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Principal Investigator: Shoucheng Zhang
Sr. Investigator(s): David Goldhaber-Gordon; Stanford University
Hari Manoharan; Stanford University

Students: Joseph Orenstein; Lawrence Berkeley National Laboratory
4 Postdoctoral Fellow(s), 7 Graduate(s), 0 Undergraduate(s)
Funding: \$804,000 (2014)

PROGRAM SCOPE

The main goals of this FWP are to discover new states of quantum matter and novel physical effects associated with the electron spin, to observe and to manipulate quantum spin degrees-of-freedom at the microscopic scale, and to design and predict materials with tailored functionality. The spin physics program investigates novel phenomena arising from spin coupling in solids. Recently, it was realized that spin-orbit coupling can lead to a fundamentally new state of matter, the topological insulator. These materials have an energy gap in the bulk, and a conducting topological state on the surface. The spin program develops theoretical concepts and experimental tools to investigate these novel effects.

FY 2014 HIGHLIGHTS

(1) A new platform for topological superconductivity. Manoharan, Orenstein, and Zhang actively worked together on the half-metallic surface state of NaCoO_2 as a platform for topological superconductivity and Majorana fermions through the mechanism of s-wave superconductivity proximity effect. Manoharan performed STM measurements on the surface states of NaCoO_2 , and distinguished the p-type doping surface region. The observed local density of states (LDOS) by STM experiments quantitatively agrees with Zhang group's *ab initio* calculations, indicating the single Fermi surface on NaCoO_2 . The single surface state was confirmed by ARPES experiments done by Yulin Chen. The magnetization of the surface states was confirmed by measurements of the magneto-optical Kerr effect by Orenstein group revealing a remnant magnetization of the state with a critical temperature $T \sim 15$ K, in agreement with T-dependent scanning tunneling spectroscopy performed by Manoharan group. (2) Quantum anomalous Hall effect theory. Zhang group has theoretically predicted the quantum anomalous Hall (QAH) effect in magnetic topological insulators. Recently, this theoretical prediction has been confirmed experimentally in Cr doped topological insulator $(\text{Sb,Bi})_2\text{Te}_3$. Zhang group published five papers on QAH effect. (3) Quantum anomalous Hall effect experiments. Orenstein, Goldhaber-Gordon, Manoharan, and Zhang actively worked together on the ferromagnetism of Cr doped topological insulator $(\text{Sb,Bi})_2\text{Te}_3$. (4) Quantum spin Hall effect. Zhang group has theoretically predicted the quantum spin Hall (QSH) effect in HgTe quantum well as well as topological insulators Bi_2Se_3 . (5) TRI topological superconductor prediction. Zhang group has theoretically proposed the concept of time-reversal invariant topological superconductivity.

EARLY CAREER: Real Time TEM Imaging of Materials Transformations in Liquid and Gas Environments

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Sr. Investigator(s):
Students: 4 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding: \$500,000 (2014)

PROGRAM SCOPE

The aim of this project is to study the physical and chemical processes in materials with high spatial resolution using *in situ* liquid or gas environmental transmission electron microscopy (TEM). Understanding how materials grow and function at the nanometer or atomic scale in their working environments is essential to developing efficient and inexpensive energy conversion and storage materials and devices. With real time imaging in liquids or gases, this project will advance environmental cell TEM development and result in better understandings of growth, mass transport and chemical reaction induced structural changes of materials during energy applications.

FY 2014 HIGHLIGHTS

The reliance of future technologies on advanced materials has spurred intense interest in solution growth of nanostructured materials owing to the substantial advantages with respect to the massive scalability required for any global energy solution. An understanding of the solution growth mechanisms of nanocrystals is critical to the design of novel materials. *In situ* study of nanoparticle growth trajectories using liquid cell TEM is a unique approach. With our recent effort, breakthroughs have been made on the study of facet development of Pt catalytic nanoparticles. With the thin liquid cells and advanced imaging detector, we were able to capture the atomic development of each individual facet. We found the widely implemented surface energy minimization rule breaks down at the nanoscale. Instead, stochastic growth dominates and the facet development is strongly influenced by surfactant ligands. This work has been published in Science Aug. 2014. This work is an excellent extension of our previous effort on the study of shape evolution mechanisms of nanocrystals. Another highlight is the *in situ* study of dendritic growth in electrochemical processes with our development of electrochemical liquid cells. The electrochemical liquid cells allow us to monitor the electrode-electrolyte interfaces and reveal unseen materials dynamics at the nanoscale. Two papers on the formation of Pb dendrites and Li dendrites have been published in Scientific Report and Nano Letters. It opens the opportunities to study many other dynamic processes including electrodeposition, electrocatalysis and so on at a great level of details which were not possible before. Additionally, we have also made significant progress on the study of structural dynamics of nanocatalysts *in situ* using gas environmental cell TEM. The recent work has been published in Nano Letters and there are multiple news reports on the achievement.

Studies of Nanoscale Structure and Structural Defects of Advanced Materials

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Students:	1 Postdoctoral Fellow(s), 3 Graduate(s), 0 Undergraduate(s)
Funding:	\$2,232,000 (2014)

PROGRAM SCOPE

The goal of this program is to understand the roles of property-sensitive nanoscale structures and defects of technologically-important materials such as superconductors, multiferroics, spintronics, and other energy related materials including thermoelectrics, batteries and catalysts. To gain a thorough

understanding we employ and advance quantitative electron diffraction, imaging, and spectroscopy techniques, including the pump-probe based ultrafast electron diffraction method. We aim at understanding the electron, spin, orbital, and lattice correlation and their interplay that control physical and chemical behavior of matter. One essential component of our program is developing advanced instruments and methods for direct measurement of materials' structural functionalities at nanoscales and comparing them with those obtained using neutrons and synchrotron x-rays. The progress of our research requires a significant resource suitable for a national laboratory setting, wherein applications to various model systems in strongly correlated oxides and energy-related materials can be demonstrated. Computer simulations and theoretical modeling are carried out to aid the interpretation of experimental data. Fabrication of thin films with tailored nanostructures is also incorporated.

FY 2014 HIGHLIGHTS

Direct observations of coherence and modality of driven interlayer-coupled magnetic vortices using high-frequency resonance current; Revealing the direct coupling between anion polarization and superconductivity in Co doped BaFe_2As_2 superconductors using quantitative electron diffraction and energy-loss spectroscopy; Revealing interface-induced nonswitchable domains in ferroelectric thin films; Direct imaging of vortex-core precession orbits and the interaction of double vortex-cores in strongly and weakly coupled tri-layered magnetic nanostructures; Identifying the origin of phonon glass–electron crystal behavior in layered thermoelectric materials; Understanding topological effect of surface plasmon excitation in gapped isotropic topological insulator nanowires; Imaging symmetry breaking of magnetic vortices before annihilation; Separating the electron and lattice contribution to the formation of charge-density-wave in TaSe_2 using ultrafast electron diffraction; Observing tunable THz surface plasmon polariton based on a topological insulator/layered superconductor hybrid structure.

EPSCoR

Institutions Receiving Grants

EARLY CAREER: Develop On-Demand Nanoplasmonic Device Concepts in a Semiconductor Compatible Hybrid System

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Funding: \$750,000 (2013-2017)

PROGRAM SCOPE

The objective for this project is to develop an on-demand nanoplasmonic platform that combines emerging oxide nanoelectronics with a low-loss semiconductor-friendly plasmonic material — graphene. In the heterostructures of Graphene/LaAlO₃/SrTiO₃, the nanoscale conducting structures at LaAlO₃/SrTiO₃ interfaces reversibly patterned by conducting atomic force microscope (c-AFM) will be used to spatially modulate the chemical potential in the top graphene layer and provide dynamic confinement and manipulations of plasmon modes in graphene. Various rewritable nanoplasmonic devices, including waveguides, active modulators, on chip light source and sensors, will be explored by c-AFM lithography and in-situ near field scanning optical microscopy. The successful development of such hybrid plasmonic platforms will enable creation of on demand nanoplasmonic devices in one single step and can potentially lead to tantalizing applications in single molecule spectroscopy, scalable solid state quantum information processing and novel plasmon probe for various interesting material quanta in condensed matter physics.

FY 2014 HIGHLIGHTS

A new material stack of Si/LaAlO₃/SrTiO₃/SiO₂/Si has been developed and studied. With thickness ratio of the stack designed by finite element simulation, the new heterostructure enhances the optical contrast of graphene by orders of magnitude comparing to the originally proposed LaAlO₃/SrTiO₃ substrate. In addition, the introduction of Si also allows the carrier density in graphene and LaAlO₃/SrTiO₃ interface to be tuned independently. A dry transfer method based on PDMS stamp has been developed to transfer a patterned graphene structure from copper foil directly onto a LaAlO₃ surface. This method eliminates the exposure of resist related chemicals to highly surface sensitive graphene or polar complex oxide (LaAlO₃), and allows high quality contacts to be formed to access graphene and LaAlO₃/SrTiO₃ interfaces separately. The reversible C-AFM lithography in presence of graphene has been successfully performed. The LaAlO₃/SrTiO₃ interface underneath single monolayer graphene can be reversibly switched between metallic and insulating states with biased conducting atomic force microscope (c-AFM) probe in contact with graphene. Small voltage applied to the conducting regions at the LaAlO₃/SrTiO₃ interface can effectively control the graphene transport with a large on-off ratio. Surface plasmon mode has been successfully observed in highly doped SrTiO₃ region by near field scanning optical microscope. The mechanism of the C-AFM lithography in the presence of

graphene as well as plasmon modes in graphene/oxide heterostructures will be the subject of next step investigations

Neutrino Oscillations in Supernovae

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Sr. Investigator(s):
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Funding: \$750,000 (2012-2017)

PROGRAM SCOPE

At the end of its life the core of a massive star collapses under its own gravity, and the star explodes as a supernova. Supernovae are crucial to the chemical evolution of the universe. They disseminate heavy elements into the Interstellar Medium inside which new generations of stars are born. Although supernovae have been observed in the last several decades, it is until recently, with the advances of computing technologies and the development of multi-dimensional supernova simulations, that the explosion mechanism of a supernova is finally (close to be) understood. However, the recent development of neutrino mixing adds a new twist to this puzzle. Neutrinos interact very weakly with ordinary matter but carry away 99% of the total energy of a supernova. The electron flavor neutrinos and antineutrinos play pivotal roles in supernova physics. It has been established by experiments that neutrinos and antineutrinos of the electron flavor can transform or oscillate into neutrinos of other flavors and vice versa. In this project we use both analytic and numerical methods, including large-scale numerical simulations, to find out the mechanism and conditions for neutrino oscillations to occur in supernovae and to study the potential impacts of neutrino oscillations on supernova physics. By understanding neutrino oscillations in supernovae we will complete an important piece for the puzzle of supernova physics and help answering some fundamental questions such as the origin of the elements.

FY 2014 HIGHLIGHTS

Two important progresses have been made in FY 2014 towards understanding (collective) neutrino oscillations in supernovae. We have developed a multi-purpose numerical package xFLAT to simulate neutrino oscillations in several physical models. Compared to the old package xFLAT is designed to utilize the vector engines of modern CPUs, and it runs efficiently on the 60-core Xeon Phi accelerator introduced by Intel recently on which we plan to run our future large-scale simulations. This numerical package was one of the highlights of the UNM booth during the SC14 conference. We have also developed a new approach, the moment expansion method, to compute neutrino oscillations in the one-dimensional (i.e. spherically symmetric) "neutrino bulb model". Compared to the traditional angle-bin method the new approach improves the efficiency by about 2 orders of magnitude. This improvement of efficiency can be essential for us to devise and carry out simulations of neutrino oscillations in multi-dimensional models. This work has been published by Journal of Cosmology and Astroparticle Physics.

Neutron Scattering Research Network for EPSCoR States

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Students: 3 Postdoctoral Fellow(s), 3 Graduate(s), 0 Undergraduate(s)
Funding: \$1,666,000 (2012-2015)

PROGRAM SCOPE

With the completion of the Spallation Neutron Source (SNS) and upgrading of the High-Flux Isotope Reactor (HFIR) at the Oak Ridge National Laboratory (ORNL) the state of Tennessee now leads the world in the capability for neutron scattering research. This project aims at directing the great impact of these facilities to researchers in the EPSCoR states, Tennessee in particular, by creating a research collaboration network around these facilities. The plan consists of two parts: (1) Direct effort to increase the user base through the travel fellowship for graduate students and faculty from the EPSCoR states to use the neutron facilities at the ORNL, and through workshops and schools on the application of neutron scattering, and (2) Research collaboration among the core participants from UTK, ORNL and other states. The EPSCoR Travel Fellowship Program started in the Phase I of this grant (2008-2012) has supported a large number of neutron facility users and workshop participants. This program is highly popular particularly among young researchers, and is the foundation of this project. We supported several educational workshops, organized one by ourselves each year, targeting non-users of neutron scattering. The core research groups participating in this project include not only researchers from Tennessee but those from Kansas, South Carolina, Puerto Rico and Louisiana, making this project a national, rather than regional, enterprise. Collaborations that were seeded by this project have grown into two major projects, one in condensed matter physics and the other in soft matter sciences. Through this project we promote the use of neutron scattering, particularly in biological and life sciences and in energy sciences, and facilitate the DOE investment in this field to impact wide fields of science and engineering. This project is administered through the Joint Institute for Neutron Sciences (JINS) of the University of Tennessee (UT) and ORNL.

FY 2014 HIGHLIGHTS

The neutron travel fellowship program continued to grow, and supported 588 total users (370 distinct users) over 6 years. At the beginning of this program we estimated the number of neutron facility users from the EPSCoR states to be about 90, half of whom were from the state of Tennessee. Thus we have succeeded in increasing the number of neutron users by a factor of four. Actually less than 10% of the fellowship recipients are from the state of Tennessee, so the number of out-of-state users has increased by more than 7 times. In August we held the fourth workshop on “neutrons for novices”, which attracted nearly 50 participants. Through this series of workshops we introduced nearly 200 participants to neutron scattering, many of whom are new neutron facility users. In the research on condensed matter physics, through collaboration with subcontractors from Kansas, Louisiana, South Carolina and Puerto Rico we advanced the neutron scattering studies of the structure of new compounds, including frustrated magnets and complex hydride. We also made advances in the study of Fe-pnictide superconductors through the discovery of strong anisotropy in spin excitation and local lattice distortions larger than the average orthorhombic lattice distortion. In the field of soft-matter physics and biological science we advanced our understanding of the role of secondary structure in rigidity,

dynamics and function through the use of inelastic neutron scattering and modeling. Water is an extremely important substance in biology. Through inelastic neutron scattering, light scattering and dielectric spectroscopy the picosecond dynamics of water was studied, and elucidated the role of hydration on protein dynamics. A new effort on membrane dynamics was started a year ago, and resulted in major advances. In particular we identified the dynamic domain formation on asymmetric membranes through small angle neutron scattering and modeling.

Fundamental Investigations of Mechanical and Chemical Degradation Mechanisms in Lithium Ion Battery Materials

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Li-Qiong Wang; Brown University
Arijit Bose; Rhode Island, University of
David Heskett; Rhode Island, University of
William Euler; Rhode Island, University of
Students: 7 Postdoctoral Fellow(s), 8 Graduate(s), 1 Undergraduate(s)
Funding: \$6,000,000 (2014-2017)

PROGRAM SCOPE

We aim to understand the mechanical and chemical degradation mechanisms and improve the cycle and calendar life of lithium ion battery materials. Our effort consists of fundamental investigations of: (i) Mechanical properties, fracture and damage in electrode materials; (ii) Chemistry and Mechanics of Solid Electrolyte Interphase (SEI); (iii) Mechanical and Chemical Integrity of Solid-Solid Interfaces in Practical Electrodes. The research project consists of closely coupled experimental, theoretical and computational investigations that complement each other, in collaboration with DOE National Laboratories and industrial partners. The first focus area deals with mechanical degradation caused by the stress fields induced by volume expansion during diffusion, phase transformations and intercalation during Li insertion and removal. Continuum and atomic scale models will be developed and validated against the experiments in order to make them predictive in more general electrode architectures. The second focus area seeks to establish a rigorous relation between the electrolyte chemistry, structure & chemical composition of SEI and its mechanical properties. A suite of experimental techniques will be employed to gain unprecedented insights, which will be complemented by Density Functional Theory (DFT) simulations of the reduction reactions. The performance of practical electrode microstructures is critically dependent on the mechanical integrity of interfaces in electrodes, particularly the active-inert interfaces and active-active interfaces. The interface mechanics is often strongly influenced by chemical factors such as Li concentration and absorbed electrolyte in the binder. The third focus area will develop a detailed understanding of solid-solid interfaces in electrodes and how electrode expansion is accommodated at such interfaces. One of the objectives is to arrive at a rational materials design for composite electrode coatings.

FY 2014 HIGHLIGHTS

Phase boundaries in Li ion battery materials play a critical role in controlling the rates at which the material can be charged/discharged and the stress induced in the particle. We developed a theoretical model to describe the roles of solution thermodynamics, mechanical stress and kinetics on the behavior of electrode particles containing propagating phase boundaries. We also obtained analytical solutions for composition and stress in elastic-plastic electrode particles containing a propagating phase boundary. The most significant implication of these predictions is that chemistry can influence the stress state in electrode particles by controlling the relative contributions from solution thermodynamics and stress to the chemical potential. Tin forms multiple Li-Sn phases during lithiation; it is essential to characterize the thermodynamics and kinetics of the phase transformations and stress generation. We subjected thin films of tin to lithiation at specific constant potentials, thus allowing only a single phase transformation to proceed at each potential in a controlled manner. We employed a kinetic model to analyze phase boundary propagation and to extract the kinetic parameters such as mobility of Li atoms and reaction rate coefficients of phase transformations at steady state, which are essential for developing numerical models for more complex particle shapes and sizes. To understand the formation of the SEI, we employed electronic structure calculations of the initial surface reactions at the electrode. We use the “computational lithium electrode” technique to model the potential-dependent elementary steps of solvent degradation on Li. We have mapped out competing reaction pathways and incorporated the voltage dependence parametrically. We studied different configurations of common solvent molecules on the lithium battery’s negative electrode. These results help understand the early stages of SEI formation that are of prime importance to battery performance.

Building Neutron Scattering Infrastructure in Louisiana for Advanced Materials

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Students:	0 Postdoctoral Fellow(s), 3 Graduate(s), 0 Undergraduate(s)
Funding:	\$4,949,000 (2014-2017)

PROGRAM SCOPE

This project seeks to build a major neutron scattering infrastructure capable of treating both soft and hard materials. The objectives of this initiative include: building a base of users of the Spallation Neutron Source (SNS) and the High Flux Isotope Reactor (HFIR) in the southern region of the USA; training of talented students and postdocs in synthesis and neutron scattering techniques who will become the next generation of neutron users; and discovery of the role of coupling of degrees of freedom that determine the emergent properties of complex materials. The scientific focus of this program is to understand the role of coupling in emergent complex materials and its impact on the structure/property relationship, and to explore how this information can be utilized or applied in the guided-design of materials with the desired properties. Our goal is to tune dominant couplings to enhance a critical property in order to derive new functionality. In particular, many of the most interesting materials display coupling both in their static and dynamical behavior, making neutron scattering (elastic and inelastic) the ideal tool to elucidate fundamental relationships. This program takes advantage of the synergy between the expertise of Louisiana’s faculty and that of the Spallation Neutron Source (SNS) and High Flux Isotope Reactor (HFIR) staff to position the team as leaders in the exploration of complex

interactions that give rise to novel phenomena. The scientific team is exploring the static and dynamic properties of transition metal compounds including transition metal oxide, silicide, and selenide/telluride systems via neutron scattering techniques that emphasize the effects of uniaxial pressure. In the soft materials systems we are investigating the effects of secondary interactions using neutron scattering on the mesoscale structure in well-defined model polymer systems as a function of polymer system type and synthetic/processing route.

FY 2014 HIGHLIGHTS

The grant was awarded in August 2014. Work completed prior to September 30, 2014 includes the following: During the first six weeks of the project we have established much of the administrative structure of the program. This includes establishing an External Advisory Committee consisting of six highly accomplished researchers with great experience in the programmatic areas of the LaCNS. We have searched for and hired a highly experienced program coordinator, established hiring searches for several postdocs and a visiting professor, and identified three graduate students that are now receiving support from this program. We have begun the processes of purchasing all of the capital equipment supported by DOE funding including commencing a competitive bid process where appropriate. In addition, we have established several collaborations between faculty participants and ORNL staff that will prove highly beneficial to the goals of the program. A seminar program focusing on neutron scattering-relevant science which hosts speakers external to the program's institutions has also been established. Weekly and biweekly meetings of the soft and hard matter teams have been established. Two faculty members of the team attended and formally presented ideas and perspectives at the SNS workshop on "Neutrons and High Magnetic Fields" at ORNL in September 2014. In addition, materials synthesis for the experiments has begun with several polycrystalline and crystalline transition metal compound samples being produced and polymeric thin films being grown.

EARLY CAREER: Modeling of Photoexcited Process at Interfaces of Functionalized Quantum Dots

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Students:	1 Postdoctoral Fellow(s), 2 Graduate(s), 4 Undergraduate(s)
Funding:	\$750,000 (2012-2016)

PROGRAM SCOPE

The long-term goal of this research is theoretically establishing the structure-property relationship of chemically functionalized semiconductor quantum dots (QDs) targeting chemical, structural, and size manipulation of their electronic and optical properties. In the realm of energy related research, advances that rely upon the use of QDs are currently limited by a lack of understanding of fundamental processes that occur at the surfaces and interfaces of these nanomaterials upon photoexcitation. The complexity of this task poses high demands on the experimental techniques used to characterize nanoscale systems. Computational modeling provides interpretations of experimental data and a better understanding of the material's properties at the atomistic level, while development of validated theoretical predictions could guide new experimental efforts. As such, this project aims to improve our understanding of the role of QD surfaces in light-driven physicochemical processes via developments and practical applications of reliable quantum chemical methodologies capable of modeling

photoinduced dynamics and spectroscopic observables in the nanosized systems and their interfaces. Specifically, it focuses on systematic computational studies of the effect that a soft layer of organic ligands, including metal-organic complexes, and a shell of a different semiconductor covering the QD surface have on the morphology, electronic structure, optical response, charge/energy transfer, and excitation dissipation in QDs. Density functional theory (DFT) and time dependent DFT (TDDFT) are coupled with quantum-classical non-adiabatic dynamics and used as the quantitative framework for computing ground and excited state electronic structures, photoexcited trajectories, and electron-phonon couplings responsible for energy-to-heat losses. Simulated results will allow for a better interpretation of experiments, and facilitate rational design of new nanostructures with desired properties.

FY 2014 HIGHLIGHTS

Our research aims to fill the gap in understanding of the role of QD surfaces in light-driven processes. Several steps were done toward this goal during this year. (I) We have benchmarked DFT methods and identified that PBE1 functional more accurately describes photophysics of functionalized QDs. (II) We revealed the role of QD-dye interactions on their electronic structure: Energy offsets in the QD/dye composites do not represent a simple difference of the isolated organometallic dyes and the QDs, which should be accounted for in experiments. (III) We determined the effect of the dye on mechanisms of the charge transfer in QD/dye composites. Change in a metal of the dye weakly affects the alignment of the electronic levels of the dye versus the QD's states. In contrast, negatively charged ligands and less polar solvents strongly destabilize the dye's occupied orbitals shifting them toward the edge of the QD valence band, thus, providing favorable conditions for the hole transfer. Thus we have determined thermodynamic conditions governing the direction of the charge transfer in photoexcited QDs passivated by Ru(II)-polypyridine dyes. (IV) Targeting design of metal-organic dyes with enhanced charge transfer properties, we have performed joined computational and experimental studies of optical properties of various Ir(III) complexes and demonstrated the practical realization of DFT predictions in rational structure-property design of molecular systems. These results were summarized in 4 journal publications and reported in 6 invited talks, plus 5 contributed presentations at the international scientific conferences. This conference was organized on topics closely related to the DOE funded project was organized. Two graduate students were distinguished by summer internships at National Laboratories. Three awards for excellence in science, including a Sloan Research Award in Chemistry, have been obtained, and two projects (one as PI) have been funded by NSF, plus one by ND EPSCoR NSF.

Resolving Reactor Antineutrino Anomaly with Strong Antineutrino Source

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Sr. Investigator(s):	
Students:	1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	\$750,000 (2013-2018)

PROGRAM SCOPE

The scope of this project is search for the sterile neutrinos in 1 eV^2 mass range using a very strong antineutrino generator. For this purpose we are preparing 5 PBq ^{144}Ce - ^{144}Pr radioactive source (as a copious antineutrino source). The source will require a sizable tungsten shield to protect humans and

detector from high rate 2.2 MeV gammas, as they produce background for neutron capture on protons as second part of IBD interaction. The source will be placed below the Borexino antineutrino detector. This large antineutrino detector will allow us to observe distance dependent oscillation flux if it is there. We expect to observe around 12,000 antineutrinos in the course of 18 months. With this measurement we will be able to fully probe the preferred parameter space for $\sim 1 \text{ eV}^2$ sterile neutrinos indicated by RAA (Reactor Antineutrino Anomaly).

FY 2014 HIGHLIGHTS

During the course of FY 2014 there was significant progress on the shielding design. Two manufacturers have been identified that are capable of producing a 2.2 ton tungsten shield that can meet safety and background suppression requirements. PI has recently hired a postdoc Koun Choi to work on the CeSO_x and she will carry out simulations to ensure that the shield provides sufficient shielding against gammas in the Borexino detector. PI visited PLANSEE factory in Germany, one of the two companies that accepted the challenge of producing the shield. Another company is Xiamen in China. No company in the world has produced such a large tungsten part and there are technological challenges involved. The companies seem confident in their ability to produce the shield. Space under Borexino has been identified and prepared for receiving the source. Areva transportation company has taken over transportation of the source and a special B type container has been identified to carry the source from Sankt Petersburg to Gran Sasso in Italy. Finally, Mayak has carried a test production run for ^{144}Ce - ^{144}Pr with about 1/15 of activity and they have started the necessary modifications to upgrade the facilities needed to produce the source.

Atmosphere to Grid: Addressing Barriers to Energy Conversion and Delivery

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John O'Brien; Wyoming, University of
Suresh Muknahallipatna; Wyoming, University of
Donglian Duan; Wyoming, University of
Shawn Wulff; Wyoming, University of
Blair Robertson; Wyoming, University of
Robert Godby; Wyoming, University of
Roger Coupal; Wyoming, University of
Matt Donnelly; Montana Tech
Dan Trudnowski; Montana Tech
Students: 1 Postdoctoral Fellow(s), 17 Graduate(s), 0 Undergraduate(s)
Funding: \$4,250,000 (2014-2017)

PROGRAM SCOPE

This project addresses the barriers to incorporating renewable energy sources into the national energy infrastructure from both technical and economic points of view. This project adopts a comprehensive multi-scale and multidisciplinary approach that considers the complete energy conversion and delivery cycle, from continental atmospheric weather events, to wind farm power production and reliability, to power grid transmission issues, and including economic drivers and impact on local and regional scales. The project is centered around three principal interdependent thrusts: 1) the development and validation of a variable-fidelity multi-scale coupled atmosphere/wind-plant modeling and control capability, 2) the development of a measurement-based transmission grid modeling capability, and 3) the development of fully integrated economic models for more diverse and variable energy generation and transmission scenarios. Improved wind plant modeling capability will provide a better understanding of complete wind farm power responses to slow and rapid transient weather events, provide information for potential wind farm turbine siting in complex terrain, and allow the design and testing of control strategies for optimizing power output and reliability of entire wind farms. At the same time, measurement based transmission grid modeling capability will result in a better understanding of power system instabilities and congestion, which are current obstacles that are exacerbated in the presence of high wind energy penetration. Economic models will provide the necessary tools for measuring the overall benefit of improvements in wind energy and power transmission technologies, while at the same time enabling informed decisions regarding investment in conventional and renewable energy sources. This project includes collaboration with wind farm operators and power companies through extensive data sharing.

FY 2014 HIGHLIGHTS

Although the project began very late in the year (August 2014), there are a few accomplishments to point out. A successful kick-off meeting was held in September 2014. A review of the proposed work was provided by a team of external reviewers, and their suggestions promise to increase the value of the work to be done. Similarly, initial setup of administrative structure to support the research efforts has been started, and graduate students have been recruited.

EARLY CAREER: Examination of Actinide Chemistry at Solid-Water Interfaces to Support Advanced Actinide Separations

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Principal Investigator: Brian Powell
Sr. Investigator(s):
Students: 1 Postdoctoral Fellow(s), 2 Graduate(s), 1 Undergraduate(s)
Funding: \$750,000 (2013-2017)

PROGRAM SCOPE

The study of the chemical and physical properties of actinide bonding and reactivity is essential for the development of an improved nuclear fuel cycle and to understand how the actinides move through the environment. This work will examine the fundamental chemical properties of actinide elements in aqueous solutions and at solid-water interfaces. Sorption of actinides to solid surfaces such as minerals and soils can limit the movement of actinides in the environment and sorption to engineered solids can

facilitate separation of actinides from other waste materials within the nuclear fuel cycle. Understanding and quantifying actinide bonding and reactivity at solid-water interfaces is needed for a wide range of applications such as advanced actinide separation schemes, waste treatment and disposal, understanding actinide behavior under geologic repository conditions, and determining the performance of actinide bearing wastes and waste facilities. A novel aspect of this work will be to examine sorption processes on a mechanistic basis and quantify the data using a standard thermochemical construct as opposed to the empirical methods commonly employed. The overarching objectives of this work are to provide a mechanistic conceptual model and a quantitative sorption model describing actinide behavior at solid-water interfaces based on a molecular level understanding of the chemical processes involved. Particular attention will be focused on understanding underlying mechanisms of actinide sorption to differing solid phases, understanding underlying mechanisms behind frequent observations of hysteretic sorption and understanding the potential formation of ternary actinide-ligand-surface complexes. The ability to predict distribution of the actinides between aqueous and solid phases will improve our overall understanding of actinide behavior in natural and engineered systems and facilitate prediction of actinide behavior in complex systems.

FY 2014 HIGHLIGHTS

Titanium-doped magnetite nanoparticles were synthesized to examine the effects of systematically increasing the Fe(II)/Fe(III) ratio in magnetite on the adsorption of light actinides with a range of oxidation states. Preliminary results indicate that increased Ti concentration (and the resulting increase in surficial Fe(II) and Ti(IV)) results in increased absorption of actinides in the pentavalent and hexavalent oxidation states at low pH (~3). These results demonstrate that 'tunable' solid phases provide control over actinide partitioning in complex aqueous solutions which may be useful in understanding actinide geochemical behavior and in the development of actinide separation processes. Graphene oxide (GO) has been explored as a novel radionuclide sorbent. Sorption of Tc(VII) is very weak in neutral pH solutions but increases drastically with increasing acid concentration up to 5M HCl. The stability of GO under these harsh conditions illustrates its potential use for Tc removal (potentially selective removal) from strongly acidic waste streams. Strong sorption of Eu(III), U(VI), Np(V), and Th(IV) to GO in solutions ranging from pH 1 to 9 have been examined using a variety of techniques including FTIR-ATR, High Resolution-TEM/EDX, and quantum mechanical modeling. The GO appears to be capable of profoundly high sorption capacities which are on the order of 10 to 100 mg actinide/g_{GO}. The results indicate sorption is likely driven by complexation with carboxylate functional groups and sequestration of trivalent and tetravalent species within the interlayers of GO sheets. Examination of actinide and Tc interactions with these two novel sorbents is providing high level detailed information regarding the chemical behavior of these ions at solid:water interfaces. Gaining a molecular level understanding of these solid:water interface reactions will help to improve our understanding of actinide behavior in natural and engineered systems.

Radionuclide Waste Disposal: Development of Multi-scale Experimental and Modeling Capabilities

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Sr. Investigator(s): Timothy DeVol; Clemson University
Stephen Moysey; Clemson University
Lawrence Murdoch; Clemson University
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Students: Zheng Chang; South Carolina State University
5 Postdoctoral Fellow(s), 15 Graduate(s), 10 Undergraduate(s)
Funding: \$5,250,000 (2014-2017)

PROGRAM SCOPE

The objective of this project is to address scientific issues limiting understanding of radionuclide behavior in natural and engineered systems. The key issues to be addressed include identifying source terms for contaminants in geologic disposal scenarios, determining the chemical speciation of contaminants, delineating the biogeochemical and physical processes through which contaminant transport is manifested, and predicting contaminant mobility across wide temporal and spatial scales. This will be accomplished through a collaborative effort between scientists and engineers at Clemson University, University of South Carolina, and South Carolina State University. The proposed research program consists of the following four integrated tasks: Task A: Origins of Radionuclide Source Terms in Legacy and Advanced Waste Forms; Task B: Biogeochemical Behavior of Radionuclides in Natural Systems: Mineral, Plant, and Microbial Interactions; Task C: Imaging and Meso-Scale Facilities to Support Radionuclide Transport Studies; Task D: Development of Advanced Reactive Transport Models. These tasks will utilize an imaging facility to be designed and implemented as part of this work. The imaging facility will provide pore to lab scale imaging of radionuclide transport through soils as well as monitor the chemical, biological, and physical changes occurring in the soils over time. Through this implementation grant, we will (1) develop an innovative, cross-disciplinary testing and imaging facility, (2) construct a meso-scale field lysimeter facility for long-term radionuclide release experiments (both of which will support of nationwide nuclear-environmental efforts), and (3) apply and experimentally verify highly integrated reactive transport models of radionuclide transport in natural and engineered systems, including vegetation. The end result of these efforts will be used to address nuclear waste issues arising from commercial nuclear energy and legacy weapons production.

FY 2014 HIGHLIGHTS

The start date for this project is August 15, 2014. Therefore, the project was only active for a few weeks of FY 2014. An all hands meeting was held August 19th and an onsite DOE review was held September 25-26th. The scope of the project was presented to DOE program managers and reviewers.

Center for Interfacial Reaction Engineering

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Sr. Investigator(s): Jeffrey Harwell; Oklahoma, University of
Steven Crossley; Oklahoma, University of
Bin Wang; Oklahoma, University of
Sanwu Wang; Tulsa, University of
Jeffrey White; Oklahoma State University
Clinton Aichele; Oklahoma State University
Brian Neeley; Oklahoma State University
Students: 6 Postdoctoral Fellow(s), 14 Graduate(s), 3 Undergraduate(s)
Funding: \$3,160,699 (2013-2016)

PROGRAM SCOPE

Investigations focus on reactive interfaces in liquid/liquid/solid systems with impact in energy applications, including biomass conversion, catalytic upgrading in liquid biphasic systems, polarity-driven selectivity, generation of H₂ through photocatalysis, and subsurface conversion in oil reservoirs at the water/oil interfaces. The four interconnected research thrusts include (a) Dynamics and structure of emulsions stabilized by nanoparticles such as nanotubes, Janus particles, and nanohybrids. Characterization under varying particle concentration, temperature, pH, water/oil ratio, flowing conditions, etc. Gel formation at very low solid concentrations is conducted with binary particles of different isoelectric points. (b) Synthesis, functionalization, and characterization of amphiphilic nanoparticles. Functionalized carbon nanotubes with varying hydrophobic/hydrophilic balance, which allows us to precisely control the location and orientation of the particles at the water/oil interface. Precise silylation of external surface minimizes the high susceptibility of hydrophilic zeolites to hot liquid water while keeping the active acid sites unaffected. Unfunctionalized zeolites lose crystallinity rapidly, but after silylation stability greatly increases without losing catalytic activity. (c) Reaction kinetics and transport phenomena in biphasic systems catalyzed by solids. Water/organic biphasic media; Fischer Tropsch synthesis, hydrogenation, hydrodeoxygenation, alkylation, photocatalytic oxidation. By properly adjusting the chemical potential of compounds, the kinetics and rate of mass transport can be finely controlled, thus controlling the selectivity of reactions in each phase. (d) Theory and spectroscopy at the water/oil/solid interfaces. Combination of FTIR, Raman, and NMR spectroscopies with DFT calculations and MD simulation has allowed us to obtain mechanistic insight on reactions catalyzed by metals, oxides, and acids occurring in the aqueous/oil media.

FY 2014 HIGHLIGHTS

Important progress has been accomplished in all four CIRE research thrusts. As a result, several publications (some involving various groups) have been obtained from work conducted under CIRE. They include 1. Chen, Damron, Pearson, Resasco, Zhang, White. "Zeolite Catalysis: Water Can Dramatically Increase or Suppress Alkane C-H Bond Activation" *ACS Catalysis*, 4 (2014) 3039 2. Weston, Venkataramani, Aichele, Grady, Harwell, Resasco, "Pseudo-solid, shear-thinning gel formation in binary dispersions of metal oxide nanoparticles at low volume fractions" *Langmuir* 30 (2014) 14982 3. Venkataramani, Aichele, "Concentrated Emulsion Characterization in Flowing Conditions" *Energy & Fuels* (2014) - DOI: 10.1021/ef5020583 4. Resasco, "Carbon nanohybrids used as catalysts and emulsifiers for reactions in biphasic aqueous/organic systems" *Chin. J. Catalysis* 35 (2014) 798 5. Shi, Faria, Pham, Resasco, "Improved Activity and Selectivity of Fischer-Tropsch Synthesis Catalysts in Water/Oil Emulsions" *ACS Catalysis* 4 (2014) 1944 6. Gebreyohannes, Neely, Gasem, "One-parameter modified nonrandom two-liquid activity coefficient model" *Fluid Phase Equilibria* 379 (2014) 196 7. Gebreyohannes, Neely, Gasem, "Generalized NRTL interaction model parameters for predicting liquid-liquid equilibrium behavior" *I&EC Research* 53 (2014) 12445. Based on the work conducted under CIRE, several of the PIs have been invited to speak in important events (ACS symposia, several universities in the US and Europe, PANIC NMR meeting, etc.). Members of CIRE have made ten contributed presentations at ACS Annual Meeting (San Francisco) and AIChE Annual Meeting (Atlanta) and submitted for upcoming NAM and APS meetings. An important development from CIRE has been a proposal to STC NSF program including 7 CIRE participants and contributors from S. Barbara, Caltech, Washington, and Princeton.

Miracles in Scattering Amplitudes: from QCD to Gravity

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Sr. Investigator(s):
Students: 2 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding: \$750,000 (2011-2016)

PROGRAM SCOPE

Proposed research in the area of theoretical high energy physics is centered around both theory and phenomenology of scattering amplitudes in quantum field theories and gravity. Recently remarkable advances have been made in this area, with a broad spectrum of results ranging from new precision predictions in QCD which will be very important for understanding Large Hadron Collider LHC data to the miraculous structures in $N=4$ Yang-Mills and $N=8$ supergravity. The goal of my research project involves deepening our understanding of gauge and gravity theories by exploring hidden structures of scattering amplitudes (ranging from integrability to twistors to the theory of motives), and using these rich structures as much as possible to aid practical calculations relevant to collider physics. These hidden structures not only help us calculate and make predictions for experimentally relevant processes but also lead to deeper understanding of fundamental properties of field and gravity theories. The funds will be used to train graduate students and postdocs.

FY 2014 HIGHLIGHTS

We continued exploring beautiful structures in scattering amplitudes. Motivated by the cluster structure of two-loop scattering amplitudes in $N = 4$ Yang-Mills theory we define cluster polylogarithm functions. We find that all such functions of weight 4 are made up of a single simple building block associated to the A_2 cluster algebra. Adding the requirement of locality on generalized Stasheff polytopes, we find that these A_2 building blocks arrange themselves to form a unique function associated to the A_3 cluster algebra. This A_3 function manifests all of the cluster algebraic structure of the two-loop n -particle maximally helicity violating amplitudes for all n , and we use it to provide an explicit representation for the most complicated part of the $n = 7$ amplitude as an example. We also investigated soft theorems in both Yang-Mills and gauge theories, providing a universal formula in arbitrary dimension. Investigation of these theorems from Ward identities of Bondi-Metzner-Sachs symmetry is under way.

Quantum Dot Sensitized Solar Cells Based on Ternary Metal Oxide Nanowires

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Yuri Dahnovsky; Wyoming, University of
Jon Pikal; Wyoming, University of
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TeYu Chien; Wyoming, University of
Students: 2 Postdoctoral Fellow(s), 6 Graduate(s), 0 Undergraduate(s)
Funding: \$1,875,000 (2013-2016)

PROGRAM SCOPE

This joint research effort on renewable energy materials at the University of Wyoming investigates the application of novel nanostructures including ternary metal oxide nanowires and semiconductor quantum dots (QDs) in QD sensitized solar cells (QDSSCs), and aims at achieving a better understanding on carrier generation, transport, and recombination in these structures. In this renewal project our first major research goal is to investigate magnetically doped quantum dots and related spin polarization effect, which could improve light absorption and suppress electron relaxation in the QDs. We will utilize both physical and chemical methods to synthesize these doped QDs. We will also study magnetically modified nanowires and introduce spin-polarized transport into QDSSCs, and inspect its impact on forward electron injection and back electron transfer processes. Our second goal is to study novel solid-state electrolytes for QDSSCs. Specifically, we will inspect a new type of polymer electrolytes based on a modified polysulfide redox couple, and examine the effect of their electrical properties on QDSSC performance. These solid-state electrolytes could also be used as filler materials for *in situ* sample fracturing in STM and enable cross-sectional interface examination of QD/nanowire structures. Our third research goal is to examine the interfacial properties such as energy level alignment at QD/nanowire interfaces using the newly developed Cross-sectional Scanning Tunneling Microscopy and Spectroscopy technique for non-cleavable materials. This technique allows a direct probing of band structures and alignment at device interfaces, which could generate important insight into the mechanisms that govern QDSSC operation. These investigations will be carried out through a close collaboration between our experimental and theoretical efforts in this project.

FY 2014 HIGHLIGHTS

1. We have synthesized Mn-doped ZnO nanowire arrays by a modified chemical vapor deposition method in order to introduce spin-polarized transport into QDSSCs.
2. Our current approach to improving the QDSSC efficiency is to investigate QDs doped with magnetic ions like Mn. In this work, we have demonstrated that pulsed laser deposition is very effective to synthesize Mn doped CdSe QDs. Mn resides on the Cd sites inside the CdSe QDs as shown in the Raman spectrum as well as depth profile of XPS. As a result of collaborative effort, improved QDSSC device performance based on CdSe:Mn QDs was obtained compared to that based on undoped CdSe QDs. On the investigation of colloidal quantum dots, we have shown for the first time that cysteine capped CdSe QDs synthesized by ligand exchange exhibit circularly polarized luminescence.
3. The use of liquid electrolyte in quantum dot-sensitized solar cells (QDSSCs) has been primarily impeded by limitation on the stability issue. We have investigated a novel solid-state polymer electrolyte based on PEO-PVDF polymer that blends with thiosulfate ($S_2O_3^{2-}$) and polysulfide (S_x^{2-}) as redox couples, allowing for an interesting way to probe the solid-state QDSSCs with new kind of redox couple different from the traditional S_2^-/S_x^{2-} in S/Na₂S aqueous electrolyte.
4. We have done extensive optoelectronic characterization of the zinc tin oxide nanowires. There is no emission from the band edge states of the nanowires, indicating that they are a direct forbidden bandgap material. Also, there is a broad defect peak in the visible which appears to be two separate peaks. We found that the fastest time constant dominates at short wavelengths but mostly disappears by 500nm as the slower time constants increase in importance. This work has been written up and is in the final internal review stages prior to submission.
5. We have calculated optical spectra and densities of states (DOS) for various CdSe and PbS quantum dots depending of sizes and shapes.

Enhancing Metabolic Flux to Photosynthetic Biofuels

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Principal Investigator: Jamey Young
Sr. Investigator(s):
Students: 0 Postdoctoral Fellow(s), 2 Graduate(s), 1 Undergraduate(s)
Funding: \$750,000 (2012-2017)

PROGRAM SCOPE

The overall objective of the project is to test new metabolic engineering and systems biology approaches for maximizing metabolic flux to biofuels in cyanobacterial hosts. The central hypothesis is that combining directed metabolic engineering approaches with global rewiring of circadian transcriptional programs will lead to enhanced biofuel productivities. ^{13}C metabolic flux analysis and metabolomic profiling will be applied to optimize cyanobacterial production of isobutyraldehyde (IBA), which is a direct precursor of isobutanol, starting from several promising strains of *Synechococcus elongatus* PCC 7942 that have been recently constructed.

FY 2014 HIGHLIGHTS

- We applied ^{13}C labeling experiments to a wild-type *Synechococcus elongatus* PCC 7942 strain (WT) and an IBA-producing strain (IBA) to quantify photoautotrophic metabolism.
- We developed a custom MATLAB-based software package called INCA (Isotopomer Network Compartmental Analysis), which automates the model construction and numerical simulation of isotopomer balance equations required for isotopically nonstationary MFA (INST-MFA). The software is publicly available at <http://mfa.vueinnovations.com>.
- By analyzing the labeling trajectories obtained from the transient $^{13}\text{CO}_2$ labeling studies using INCA, we were able to map the flow of carbon in the WT and IBA strains.
- Based on the ^{13}C flux analysis results, we have identified a potential bottleneck in central carbon metabolism that limits IBA production.
- We have constructed several mutant strains that overexpress enzymes needed to bypass this potential bottleneck and are currently assessing the impact of these overexpressions on IBA production.

Publications: [1] Adebisi, A.O., Jazmin, L.J., Young, J.D. " ^{13}C flux analysis of cyanobacterial metabolism". *Photosynthesis Research*, in press (2014). [2] Young, J.D. "INCA: A computational platform for isotopically nonstationary metabolic flux analysis". *Bioinformatics* 30:1333-1335 (2014). [3] Jazmin, L.J., O'Grady, F. Ma, D.K. Allen, J.A. Morgan, J.D. Young, Chapter 12: Isotopically Nonstationary MFA (INST-MFA) of Autotrophic Metabolism. *Methods in Molecular Biology*, 1090, 181-210, eds. M. Dieuaide-Noubhani and A.P. Alonso, Springer NY (2014). [4] Young, J.D., D.K. Allen, and J.A. Morgan, Chapter 7: Isotopomer Measurement Techniques in Metabolic Flux Analysis II: Mass Spectrometry in Plant Metabolism. *Methods in Molecular Biology*, 1083, 85-108, ed. G. Sriram, Springer NY (2013). [5] Jazmin, L.J., Young, J.D. Chapter 18: Isotopically Nonstationary ^{13}C Metabolic Flux Analysis. *Methods in Molecular Biology*, 985, 367-390, ed. H. Alper, Springer NY (2013).

EARLY CAREER: Growth and Properties of New Epitaxial Metal/Semiconductor Nanocomposites

Institution: Delaware, University of
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Principal Investigator: Joshua Zide
Sr. Investigator(s):

Students: 0 Postdoctoral Fellow(s), 2 Graduate(s), 3 Undergraduate(s)
Funding: \$750,000 (2012-2016)

PROGRAM SCOPE

Nanocomposites consisting of rare-earth monpnictide nanoparticles (e.g. ErAs) within III-V semiconductors represent a useful composite material for a variety of applications. The incorporation of nanoparticles into semiconductors can pin the Fermi level, drastically altering the electronic properties in ways that are fundamentally different from conventional doping. This can reduce carrier lifetimes and also controllably change electrical conductivity depending on the matrix and composition of the nanoparticle. Additionally, nanoparticles scatter phonons, reducing thermal conductivity. These materials have been studied using molecular beam epitaxy (MBE)-grown materials and have been shown to be promising for myriad (opto)electronic and energy conversion applications. The epitaxial relationship between the crystal structures of the nanoparticles and matrix creates high quality interfaces, allowing the study of charge transfer mechanisms in nanostructured electronic composites. While prior work by MBE has enabled significant advances in the understanding of a subset of this class of composite materials, the hallmarks of MBE-grown material are a lack of flexibility in composition, a slow growth rate, and very high cost. To these ends, this project is focused on creating epitaxial nanocomposites via a hybrid approach in which nanoparticles are produced using inert gas condensation (IGC) and incorporated epitaxially into semiconductor films using liquid phase epitaxy (LPE). This hybrid approach has several advantages. First, there is considerable flexibility in what materials are grown because the nanoparticles are produced separately. Many different compositions can therefore be explored. This new approach also allows growth rates of micrometers per minute rather than micrometers per hour, thus allowing thicker films and scaling of materials. Finally, this approach can be generalized; we hope to establish a new paradigm in nanocomposites for electronic materials.

FY 2014 HIGHLIGHTS

The past fiscal year was a critical time in this project, as the Inert Gas Condensation (IGC) system became fully operational. Accordingly, erbium arsenide (ErAs) nanoparticles were produced and characterized, and techniques to control particle production, collection, and characterization have been refined. Specifically, switching to a laser ablation approach for the evaporation of both the rare earth (erbium) and the group V species (arsenic) has permitted excellent control over relative evaporation rates by defocusing the laser spot. Under one set of growth conditions, we have obtained particles with a mean diameter of approximately 4nm with a standard deviation of approximately 1nm. Changing helium pressure and evaporation rate permits tuning of particle size distribution, but we are still working to thoroughly characterize this effect. Additionally, we have found that collected particles do not oxidize as readily as initially expected. This result is both fortuitous (as it permits more flexible characterization of particles) and also sensible given the quite small size of the particles. We are currently working on characterizing particle morphology and determining how to control size. Additionally, because ErAs is anti-ferromagnetic (albeit with a low Neel temperature of 4K), we are exploring opportunities to determine how magnetic properties of antiferromagnetic materials scale with particle size. In this past year, we have also rebuilt the liquid phase epitaxy system and determined the conditions required to grow high-quality GaAs. Our most recent growths appear to be high-quality, thick (>10 micrometer), epitaxial GaAs on GaAs, and we are therefore now ready to incorporate nanoparticles into films. We expect rapid progress to continue in calendar year 2015 building on our efforts from previous years.

Experimental Condensed Matter Physics

Institutions Receiving Grants

Spin Effects in Magnetic and Non-Magnetic 2D Correlated Insulators

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Principal Investigator: Philip Adams
Sr. Investigator(s):
Students: 1 Postdoctoral Fellow(s), 1 Graduate(s), 1 Undergraduate(s)
Funding: \$180,000 (2014)

PROGRAM SCOPE

Our experimental research program is focused on the magneto-transport, non-equilibrium relaxation, and spin-resolved density-of-states properties of highly disordered two-dimensional paramagnetic, ferromagnetic, and superconducting systems. The specific research agenda of the program is organized into three separate but related areas. The first is studies of disorder and correlation effects in superconducting Al and V films that have been subjected to high Zeeman fields. We are primarily interested in what role local spin-triplet fluctuations play in determining the nature of the superconductor-insulator transition in these systems. The second class of systems that we study is represented by ultra-thin CR₃ magnetic films (R = Ni, Co, Fe) formed via e-beam deposition from arc-melted buttons of these metastable, covalently bonded compounds. When made sufficiently thin, these films they exhibit a correlated insulator phase that is similar to what we have observed in homogeneously disordered, non-magnetic, Be films. In addition to the conductivity, we can follow the magnetic behavior via the anomalous Hall effect and spin polarized tunneling as the films are pushed to higher and higher sheet resistance. The third class of systems is proximity structures comprised of non-magnetic/ferromagnetic bilayers. We have developed spin-resolved tunneling probes that give us a direct measure of the proximity-induced exchange field in non-magnetic component of the bilayers.

FY 2014 HIGHLIGHTS

We have just completed a study of the non-equilibrium behavior of disordered superconducting Al films in high Zeeman fields. We find that, in moderately disordered films, with sheet resistances of a few hundred ohms, large avalanches occur on the superheating branch of the critical field hysteresis loop. In contrast, the transition back into the superconducting phase (i.e., along the super-cooling branch) is always continuous. The fact that the condensate follows an unstable trajectory to the normal state suggests that the order parameter in the hysteretic regime is not homogeneous. We believe that the asymmetric avalanche behavior may, in fact, be a manifestation of a disordered spin polarized superconducting phase. In a separate project, we documented a magnetic field-pulse memory effect in the temperature-dependent magnetization of Tb₃₀Ru_{6.0}Sn_{29.5}, a spin-glass material having a newly identified structure type. Tb₃₀Ru_{6.0}Sn_{29.5} exhibits a glassy magnetization component of 2290 emu/mol-Tb, which represents over 84% of its total saturation magnetization. We showed that when a magnetic field pulse of a few hundred gauss is applied to the sample as it is cooling, the system retains a memory of the temperature at which the pulse was applied. Upon warming, the imprinted memory is observed as a precipitous drop in magnetization at the pulse temperature. We believe that spin-glass behavior

arises from competing interactions between the many non-equivalent magnetic sites in the complex crystal structure. Indeed, this compound has more than 100 atoms in its unit cell, with 11 inequivalent Tb sites. Unlike more traditional spin-glasses, the dynamics do not appear to be related to geometric frustration and/or structural disorder.

Heavy Fermions, Quantum Criticality, and Unconventional Superconductivity in Filled Skutterudites and Related Materials

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Principal Investigator: Bohdan Andraka
Sr. Investigator(s):
Students: 0 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

Performed research was on unconventional superconductivity and the relationship between superconducting and normal state properties. The focus was $\text{PrOs}_4\text{Sb}_{12}$, first discovered heavy fermion Pr-based superconductor which exhibits two superconducting transitions. This is one of two materials only known to have two superconducting transitions, and which remains a subject of a controversy and general interest of physics community. Existence of small crystals with a single superconducting transition leads to a consensus that the upper superconducting transition is extrinsic. We have continued broad material investigation and characterization of different $\text{PrOs}_4\text{Sb}_{12}$ samples to search for correlations between existence of the upper superconducting transition and quality of material. Specific heat, dc- and ac-magnetic susceptibility and electrical resistivity were primary experimental techniques.

FY 2014 HIGHLIGHTS

1. We were able to reproduce crystals with a single superconducting transition at T_{c2} (~ 1.75 K) in bulk-type measurements such as specific heat.
2. Single T_c samples had systematically lower RRR ratios than samples with a double superconducting transition implying their inferior quality.
3. As opposed to the accepted model, the suppression of superconductivity at T_{c1} is via the reduction of the size of the superconducting anomalies, e.g. in specific heat, and not by the reduction of T_{c1} itself.
4. The imaginary part of ac-susceptibility showed two peaks for materials with two superconducting transitions, implying inhomogeneous coexistence of two superconducting transitions.
5. We have concluded that both superconducting phases are intrinsic to $\text{PrOs}_4\text{Sb}_{12}$ and most likely are due to electronic inhomogeneities associated with near degeneracy of lowest crystal field levels.
6. Crystals with a single superconducting transition had linear $H_{c2}(T)$ variation near T_c , when measured by bulk (specific heat) method. This is contrary to the accepted believe derived from resistive measurements.

Experimental Studies of Correlations and Topology in Two Dimensional Hybrid Structures

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Students: 1 Postdoctoral Fellow(s), 0 Graduate(s), 2 Undergraduate(s)

Funding: \$160,000 (2014)

PROGRAM SCOPE

Electrons moving through the transistor channels that empower today's semiconductor-based electronic devices do not move in straight lines. This is because they are perpetually being scattered by a host of imperfections and vibrations, which put a strict limit on the electron speed and dissipate their energy by generating heat. It was recently realized that this does not have to be so. Electrons moving through graphene – one atom-thick crystals of carbon – or on the surface of the so called topological insulators, are immune to such collisions. In these materials the electrons behave like massless particles, also known as Dirac fermions, and can move along at a constant high speed in straight lines, just like photons do, over large distances corresponding to tens of thousands times the inter-atomic spacing. This is a proposal to explore electronic properties and possible device applications that arise in graphene and topological insulators due to their unusual electronic properties and topology. We will focus on phenomena that rise when these materials are combined in sandwich structures or brought in proximity with other types of electronic systems. Such heterostructures are expected to host novel phenomena that have no parallel in traditional electron systems. The research topics that will be addressed in this work include: i) effect of screening on the electronic properties of magnetically induced one dimensional chiral edge states in the quantum integer and fractional quantum Hall regime will be studied in sandwiches of graphene with boron-nitride and conducting electrodes; ii) stacking-induced modification of the electronic density of states including twist-induced van Hove singularities, correlated phases and twist-induced slowdown of the Fermi velocity; iii) electron light-like propagation and diffraction effects at boundaries; iv) induced superconductivity in graphene and topological insulators.

FY 2014 HIGHLIGHTS

This project addresses open questions on the emergence of novel electronic properties that arise in low dimensional materials due to the interplay between reduced dimensionality, incomplete screening, boundaries and proximity between different electronic states of matter. Our current focus is thin layers and interfaces including graphene, MoS₂ and stacked hybrid structures. We developed sample preparation and fabrication techniques and characterization tools that allowed us to probe the electronic properties of two-dimensional electron systems and to follow their evolution with distance from an edge, with magnetic field, doping and gating. The characterization techniques include scanning tunneling microscopy, scanning tunneling spectroscopy, Landau level spectroscopy, atomic force microscopy, Raman spectroscopy.

“Screening Charged Impurities and Lifting the Orbital Degeneracy in Graphene by Populating Landau Levels.” *Physical Review Letters*, 112, 036804 (2014). Editor's Choice It is well known that impurities leave their mark on the thermodynamic, transport and optical properties of 2D electron systems often preventing the formation of many-body quantum phases such as fractional quantum Hall states. But experimentally, the connection between the microscopic characteristics of the impurity, screening by the environment and the electronic properties of the system is still largely unexplored. In this work we studied an isolated charged impurity in graphene and obtained direct evidence of the close connection between the screening properties of a 2D electron system and the influence of the impurity on its electronic environment. Using scanning tunneling microscopy and Landau level spectroscopy we demonstrated that in the presence of a magnetic field the strength of the impurity can be tuned and controlled by a gate voltage.

Novel Temperature Limited Tunneling Spectroscopy of Quantum Hall Systems

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Funding: \$525,000 (2014-2017)

PROGRAM SCOPE

The “single particle” spectrum obtained from techniques such as photoemission or tunneling spectroscopy is among the most fundamental quantities in theories of highly interacting systems, answering the question, “at which energies can electrons be added to (or removed from) the system?” In a number of scientifically exciting and technologically important electronic systems, it has proven very difficult to achieve accurate quantitative determination of this single-particle spectrum. Among these is the two-dimensional (2D) electron system in semiconductors and in graphene. A means of spectroscopy that injects single electrons can reveal how a newly added electron is incorporated in the quantum states that produce novel electronic properties in these systems. This work studies the behavior of 2D electrons in high magnetic fields using of a unique spectroscopic technique, time domain capacitance spectroscopy (TDCS). TDCS injects or ejects electrons from the 2D system by inducing electron tunneling from hundreds of thousands of small electrical pulses. It measures the single-particle spectrum of the 2D electron system with negligible electron heating, even when the in-plane conductivity of the system vanishes. The work applies TDCS to a number of quantum Hall systems and develops a new charge detection scheme for TDCS using single electron transistors. This new method can provide high-resolution spectra of small graphene samples in the quantum Hall regime and in the recently observed “Hofstadter Butterfly”. TDCS will also be used to study the very low temperature behavior of the semiconductor two-dimensional electron systems in high magnetic fields in the regime of the fractional quantum Hall effect. TDCS can grow to be applied to technologically important systems such as high- T_c superconductors, single molecules, topological insulators, and spintronics systems to provide fundamental data on the electronic properties of these materials.

FY 2014 HIGHLIGHTS

Our work in this year has moved forward primarily in two areas: (1) development and measurements of graphene structures with the ultimate goal of performing TDCS experiments on them and (2) measurement of quantum Hall systems in GaAs quantum wells. Our graphene work resulted in a remarkable observation. In transport and capacitance measurements performed on ultra-clean graphene samples with a large in-plane magnetic field, we observed a novel quantum spin Hall (QSH) state. The QSH state is a fascinating state of matter in which the electronic transport is quantized and current is carried by two pairs of counter-propagating, spin-polarized edge modes. Its theoretical prediction and subsequent experimental discovery in an uncommon type of semiconductor quantum well developed from an early prediction of its existence in graphene arising as a consequence of spin-orbit coupling. In an alternative proposal, an exact analog of the QSH state had been proposed to exist in graphene, but unambiguous demonstration of this state has been hindered by lattice-scale Coulomb interactions, which favor valley rather than spin polarization. Our application of a large in-plane magnetic field sufficiently enhanced the Zeeman energy sufficiently to overcome Coulomb interactions, allowing direct observation of the novel QSH state and along with interesting new behaviors of the

conductivity at the sample edges. In our work in GaAs semiconductors, we have performed TDCS measurements of quantum wells containing 2D holes down to 20mK, a temperature significantly colder than our prior studies. At the lowest temperatures, we observe a sharp feature in the spectrum that is anti-symmetric in energy and density about filling factor 1. Analysis of the quasiparticles dynamics is consistent with a picture in which holes are dressed by interactions with bosonic degree of freedom that we attribute to the Goldstone mode emergent from crystalline order of the charged quasiparticles.

High Magnetic Fields as a Probe to Unveil the Physical Properties of the Newly Discovered Fe Oxypnictide Superconductors and Related Compounds

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PROGRAM SCOPE

The Fe based superconductors are generally accepted to display a superconducting pairing mechanism mediated by antiferromagnetic spin-fluctuations which in these multi-band systems is predicted to lead to a gap of s-wave symmetry and whose wave function changes its sign when going from hole-like to the electron-like cylindrical Fermi surfaces. Our current work revealed evidence for i) additional phases within the superconducting state of some of these compounds and possibly ii) time reversal symmetry superconducting states. Objectives i) To expose evidence for an additional superconducting state at high fields in the $\text{Fe}_{1+y}\text{Te}_{1-x}\text{Se}_x$ series through thermodynamic measurements and map its phase diagram. ii) Similarly, given our magnetic torque data which indicates the presence of a sharp phase transition preceding H_{c2} in extreme high quality samples of URu_2Si_2 , map its entire phase diagram as a function of field orientation and temperature by exposing its magnetic and thermodynamic properties. iii) Given the anomalous magnetic like irreversibility observed in the superconducting state of LiFeAs at high fields, which corresponds to potential evidence for broken time reversal symmetry in a superconducting state, to collect additional evidence for its existence through an array of experimental techniques. We also propose to clarify if this state is induced by the external field. v) To fully map the geometry of the Fermi surface of this compound in an attempt to elucidate what seemingly are strong discrepancies with band structure calculations. This would allow the development of theoretical models explaining its pairing symmetry which might clarify the origin of the anomalous irreversibility. vi) Given the extremely high upper critical fields observed by us in $\text{Ta}_2\text{Pd}_{0.85}\text{S}_5$, we propose to explore the possibility of observing superconductivity in other members of this family but in samples synthesized by us.

FY 2014 HIGHLIGHTS

1) Published a detailed de Haas van Alphen study in LiFeAs unveiling additional, small and nearly isotropic Fermi surface sheets in LiFeAs single crystals, which ought to correspond to hole-like orbits, as previously observed by ARPES. Our results conciliate the apparent discrepancy between ARPES and the previous dHvA results. The small size of these Fermi surface pockets suggests a prominent role for the electronic correlations in LiFeAs . The absence of gap nodes, in combination with the coexistence of quasi-two-dimensional and three-dimensional Fermi surfaces, favors a s-wave pairing symmetry for LiFeAs . 2) Reported a Shubnikov-de Haas (SdH) effect study on the pnictide parent compounds EuFe_2As_2

(Eu122) and BaFe₂As₂ (Ba122) grown by In-flux. 3) Published evidence for a field-induced quantum phase transition associated with the suppression of the spin-density wave in CeCu₂Ge₂. This transition leads to a remarkable effective mass renormalization for fields along the a-axis and to a cascade of field-induced transitions of unknown origin 4) Submitted experimental evidence for a field-induced quantum phase transition associated with the quadrupolar order degrees of freedom in PrV₂Al₂O. 5) Observed the realization of the axial anomaly in quasi-two-dimensional metal. The axial anomaly leads to the violation of separate number conservation laws for left- and right-handed massless chiral (or Weyl-) fermions. To date, there is no concrete experimental realization of a Weyl semi-metal or unambiguous evidence for this field-induced phenomenon. We observed a very large negative magnetoresistance in the extremely clean quasi-two-dimensional metal PdCoO₂. Our experimental study provides strong support for a scenario where this unconventional response results from the axial anomaly of field-induced quasi-one-dimensional conduction channels. The observation of this effect would demonstrate that the axial anomaly is a general feature of clean metals.

Electromagnetic Response of Correlated Electron Systems

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Funding: \$150,000 (2014)

PROGRAM SCOPE

The proposed program was focused on two classes of novel electronic systems: nickelates and graphene. Both classes of materials feature a wealth of new physical phenomena that are yet to be understood. Both classes of materials also hold great promise for technological applications. Therefore the proposed program allowed the PI to explore and exploit novel effects arising in these systems from complex many-body effects. The IR nanoscopy studies were aimed at the systematic investigation of role of electronic phase separation in the insulator-to-metal transition region in nickelates. Specifically, near-field IR experiments will be performed for a series of ultrathin films of NdNiO₃ and superlattices based on LaNiO₃. The electronic properties of these compounds can be controlled through strain and epitaxy. The proposed work on nickelates provided the most complete experimental picture of emergence of the metallic state in this prototypical family of correlated oxides. The graphene component of the program will focus on the methodical examination of the electronic and plasmonic response using in-house nanoscopy instrumentation as well as IR microscopy facility at the Advanced Light Source (ALS). The role of electronic correlations and many-body effects in graphene is an important unresolved problem. The PI investigated a new generation of graphene samples including specimens on BN substrates and also free-standing, suspended graphene. This work will help to ascertain the roles played by disorder and many-body effects in the intrinsic properties of graphene.

FY 2014 HIGHLIGHTS

The PI investigated hexagonal boron nitride (hBN): a common substrate material for high quality graphene. This work has resulted in the discovery of phonon polariton waves in hBN (Science 2014). Phonon polaritons are collective modes that originate from coupling of photons with optical phonons in polar crystals. Phonon polaritons in hBN reveal strong confinement quantified by the ratio of the IR

wavelength λ_{IR} to the polariton wavelength λ_p : $C=\lambda_{IR}/\lambda_p=40$. Prior to work of the PI on hBN, intriguing and potentially technologically significant nano-photonics effects in this prototypical atomic crystal had not been anticipated. These first data of propagating phonon polaritons in hBN call for the systematic studies of these enigmatic waves that are of high interest for fundamental physics as well as for applications in sub-diffractive optics/photonics.

Probing Nanocrystal Electronic Structure and Dynamics in the Limit of Single Nanocrystals

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PROGRAM SCOPE

Semiconductor nanocrystals (NCs) have been incorporated into a broad array of optoelectronic devices, including solar photovoltaics, LEDs, and downshifters. Given the potential impact of devices that use NCs as a functional material in the energy field, it is crucial to understand at a very basic level the optical physics of NCs. Without such understanding, designing novel structures, novel device architectures, and understanding the potential and limitations of present materials and devices is haphazard at best. This project consists of a set of critical and ambitious studies of nanocrystal electronic structure and dynamics, largely at the single-NC level, including: (1) utilizing a novel single molecule characterization technique that we have developed, Photon-Correlation Fourier Spectroscopy (PCFS), to reveal the intrinsic single-NC spectrum and its dynamics at time scales ranging from 30 nanoseconds to hundreds of seconds, as a function of temperature, directly in solution or fixed on a substrate, and using this to characterize interactions between single nanocrystals and their environment; (2) probing the dynamical and spectral properties of multiexcitons, as a function of temperature and through the development of solution and n^{th} -order Photon Correlation Spectroscopy (nPCS) for higher order multiexcitons ($n>2$); (3) applying PCFS and single-NC photon correlation methods to shortwave infrared (SWIR) emitting NCs that have a band gap matched to the solar spectrum (e.g. PbS, PbSe, and InAs NCs) to extract fundamental intrinsic NC spectral and dynamical properties; and (4) probing the dynamics of fluorescence intermittency to elucidate the effect of NC structure on fluorescence “blinking” and to understand mechanistically the connection between ensemble and single-NC emission properties.

FY 2014 HIGHLIGHTS

In FY 2014, we focused on four projects that advance our understanding of the fundamental photophysics of semiconductor nanocrystals (NCs). First, we leveraged our expertise in solution-phase photon correlation Fourier spectroscopy (S-PCFS) to study the average intrinsic fluorescence lineshape of single NCs. The single-NC lineshape is an important observable because it reports on the vibrational coupling between NCs and their environment. S-PCFS reveals this lineshape with high spectral resolution and signal-to-noise, and without the confounding effects of photo-charging and spectral diffusion. Our efforts, the subject of a manuscript in preparation, have shown that NC exciton-vibrational coupling is highly affected by surface effects and is less affected by NC size. Second, we constructed a new PCFS setup to study infrared-emitting materials. Infrared-emitting NCs are promising optical materials well-matched to the solar spectrum. However, their basic optical physics are not well-understood because of

the lack of sensitive infrared detectors. The recent development of superconducting nanowire single photon detectors has provided an opportunity to access the shortwave infrared optical regime. Third, we developed a new technique to measure the average biexciton quantum yield of a sample of NCs. Although previously difficult to measure experimentally, the biexciton quantum yield is an important parameter for NC fluorescence performance under high excitation flux. Our new method, recently published in Nano Letters, provides a convenient, reliable, and precise method for characterizing the effect of synthesis on the biexciton quantum yield. And finally, we contributed a review paper in Chemical Society Reviews that exhaustively documents the broad array of single-molecule techniques available to study the optical properties of NCs. This review serves as a pedagogical resource for newcomers to the field.

EARLY CAREER: Interface-Driven Chiral Magnetism in Ultrathin Metallic Ferromagnets: Towards Skyrmion Spintronics

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Funding: \$750,000 (2014-2018)

PROGRAM SCOPE

Magnetic skyrmions are localized chiral magnetic textures in the form of nanoscale vortices or bubbles that are topologically protected from being 'unwound'. Their topological nature gives rise to rich behaviors including ordered lattice formation, emergent electrodynamics and robust current-driven displacement at remarkably low current densities. However, magnetic skyrmions have so far been restricted to just a few materials and observed only at low temperatures, limiting the experimental accessibility and technological application of these unique topological objects. This project aims to realize magnetic skyrmions at room temperature in a new class of engineered chiral ferromagnets that exploit broken mirror symmetry at interfaces to generate helical magnetic order. Ultrathin magnetic heterostructures will be engineered and patterned into laterally-confined nanostructures in which skyrmions can be stabilized, manipulated, and detected for the first time under ambient conditions. Static and dynamic properties will be examined using advanced x-ray imaging and nanoscale electrical probes to provide a fundamental understanding of topological magnetic phases. The interactions between magnetic skyrmions and electron charge and spin currents will be studied to identify fundamental new physics and enable device applications. These experimental studies, supported by detailed modeling, will help launch a new subfield of skyrmion-based spintronics in which individual skyrmions can be used to encode, store, and transport information in high-performance, low power memory and logic devices.

FY 2014 HIGHLIGHTS

Since the project start date of 8/15/2014, we have successfully fabricated and characterized multilayers of Pt/Co/Ta with strong Dzyaloshinskii-Moriya interaction, and performed magnetic transmission x-ray microscopy imaging that provides the first observation of a skyrmion lattice at room temperature in an ultrathin film. In very recent work, we examined the domain structure in films and micro/nanostructures, to confirm a strong antisymmetric (Dzyaloshinskii-Moriya) interaction in these

films, showing that this strong interaction is responsible for the observed behavior. Finally, we have successfully created trains of skyrmions in a magnetic nanostrip and imaged their displacement by current, driven by the spin Hall effect. These results are currently being written up for journal submission.

Nonlinear Transport in Mesoscopic Structures in the Presence of Strong Many-Body Phenomena

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PROGRAM SCOPE

On approaching the microscopic realm from the classical world one enters an intermediate, “mesoscopic”, regime, in which rich quantum-mechanical behavior may be manifested by systems with large numbers of interacting particles. The study of physics on this mesoscopic scale has a long history of informing the development of condensed-matter physics. At the same time, this field remains fertile for fundamental discovery, most notably by addressing issues at the nexus of two distinct fields – nonequilibrium quantum transport and many-body physics. It is the exploration of novel phenomena in these regimes that provides the overarching motivation for this project. More specifically, we address important fundamental questions, such as: how are the many-body interactions of carriers modified when their motion is strongly confined on the nanoscale; how are the quantum states of isolated mesoscopic structures affected when they are coupled to an external environment; can such an environment mediate a coherent coupling between different structures, and; what is the nature of carrier transport in such systems under strongly-nonequilibrium conditions? To address these questions, we study mesoscopic transport in a variety of semiconductor nanostructures, which are implemented in high-quality gallium arsenide heterostructures, or by using an emergent material, graphene, as the carrier host. We bring novel approaches to the study of this problem, most notably by implementing transient electrical measurements that probe transport in mesoscopic systems in real-time. While the primary focus of our studies is on achieving a fundamental understanding of the complex quantum-transport phenomena that emerge at the mesoscopic scale, this project also has potential implications for attempts to develop future nanoelectronic technologies.

FY 2014 HIGHLIGHTS

We have two major accomplishments to report from 2014: (1) 'Formation of a protected sub-band for conduction in quantum point contacts under extreme biasing', *Nature Nanotechnology* vol. 9, 101 (2014). Managing energy dissipation is critical to the scaling of nanoelectronics and to the development of novel devices that use quantum coherence to achieve enhanced functionality. To this end, strategies are needed to tailor the electron-phonon interaction, which is the dominant mechanism for cooling non-equilibrium ('hot') carriers. Here, we showed a surprising behavior, in which strong electron-phonon scattering can instead be used to generate a robust mode for electrical conduction in quantum point contacts, driven into extreme non-equilibrium by nanosecond voltage pulses. When the amplitude of these pulses is much larger than all other relevant energy scales, strong electron-phonon scattering results in the spontaneous formation of a narrow current filament that conducts current with little

backscattering. This collective non-equilibrium mode may provide an effective means to manage heating in nanoscale devices. (2) 'Tuning the Fano resonance with an intruder continuum', Nano Lett. vol. 14, 788 (2014). In this work, we established the possibility of achieving strong tuning of Fano resonances, by allowing their usual two-path geometry to interfere with an additional, "intruder", continuum. As the coupling strength to this intruder is varied, we predicted strong modulations of the resonance line shape that, in principle at least, may exceed the amplitude of the original and Resonance (FR) itself. For a proof-of-concept demonstration of this phenomenon, we constructed a nanoscale interferometer from nonlocally coupled quantum point contacts and utilized the unique features of their density of states to realize the intruder. This general scheme for resonant control should be broadly applicable to a variety of wave-based systems.

Novel Behavior of Ferromagnet/Superconductor Hybrid Systems

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PROGRAM SCOPE

The interplay between superconductivity and ferromagnetism gives rise to a number of new physical phenomena. This project focuses on the unusual proximity effects that occur when conventional superconducting (S) materials are placed in contact with ferromagnetic (F) materials. Because of the strong exchange field, the electron pair correlations in F oscillate and decay rapidly with increasing distance from the S/F interface. A decade ago it was predicted that a new type of pair correlations, with spin-triplet symmetry, could be induced in S/F systems in the presence of certain kinds of magnetic inhomogeneity. Those pair correlations penetrate deeply into ferromagnetic materials; hence they are sometimes called "long-range triplet correlations," or LRTC. Our group was among the first to obtain convincing experimental evidence for the LRTC in S/F systems, in 2010. We fabricated Josephson junctions containing three ferromagnetic layers, and observed that the supercurrent persisted as we increased the thickness of the middle F layer well beyond what a conventional spin-singlet supercurrent could penetrate. Since then we have been working to understand better the signatures of the LRTC in a variety of experimental situations, as well as how to optimize and control generation of the LRTC.

FY 2014 HIGHLIGHTS

Since 2010, several groups around the world have been trying to observe long-range spin-triplet superconducting correlations in a variety of systems. Surprisingly, nobody has successfully demonstrated what would be the most dramatic confirmation of the theory, namely, control of the supercurrent in a Josephson junction by changing the relative orientations of the various ferromagnetic layers inside the junction. Such control could occur in one of two ways in a junction containing three ferromagnetic layers: 1) by rotating the magnetization of one of the layers by 90 degrees, one should be able to turn the spin-triplet supercurrent on and off; 2) by rotating the magnetization of the one of the layers by 180 degrees, one should be able to change the junction from a "0" junction to a "pi" junction. (In a "pi" junction, the ground state phase different across the junction is pi, and the current-phase relation has a negative sign relative to the standard relation observed in a "0" junction.) Some progress

toward these goals was achieved by us in 2012, and another step was taken recently by the group of Mark Blamire at Cambridge. We are current working toward both of these goals. To observe the change from 0 to π , we fabricate SQUID samples (SQUID = Superconducting Quantum Interference Device) containing two junctions. We have observed evidence for 0- π switching in such devices, but the magnetic behavior we have observed so far has not been sufficiently reproducible to allow us to make a strong claim. Hence we have not yet published these results. We are putting much effort into characterizing both strong and weak ferromagnetic materials, to help us better control the magnetic states inside our junctions.

Raman Spectroscopy of Iron Oxypnictide Superconductors

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

The objectives of project are to investigate the manner in which charge, spin and lattice coupling and dynamics evolve through various phases of iron oxypnictide superconductor families of materials by employing electronic, magnetic, and phononic Raman (i.e., inelastic light scattering) spectroscopy, and to clarify the microscopic origin of unconventional superconductivity and magnetism in these compounds.

FY 2014 HIGHLIGHTS

(1) The understanding of the phase diagram of iron based superconductors (FeSC) [2-5]; (2) The discovery of novel collective modes in FeSC [2,4]; (3) The elucidation of the superconducting “glue” in FeSC [2-5]; (4) Determination of the SC gap in $K_{0.75}Fe_{1.75}Se_2$, $BaFe_{1.9}Pt_{0.1}As_2$ and $NaFe_{1-x}Co_xAs$ superconductors [2-4]; (5) The establishment of the “Hidden Order” parameter in URu_2Si_2 heavy fermion superconductor [1]. The recent publications from DOE support include: [1] Kung, H.H., Baumbach, R.E., Bauer, E.D., Thorsmolle, V.K., Zhang, W.L., Haule, K., Mydosh, J.A. and G. Blumberg. (2014) Chirality density wave of the ‘hidden order’ phase in URu_2Si_2 . ArXiv e-prints <http://arxiv.org/abs/1410.6398> Report article to be published in Science. [2] Khodas, M, Chubukov, A.V. and Blumberg G. Collective modes in multiband superconductors: Raman scattering in iron selenides. Phys. Rev. B, 245134 (2014). [3] Ziemak, S., Kirshenbaum, K., Saha, S.R., Hu, R., Reid, J.-P., Gordon, R., Taillefer, L., Evtushinsky, D., Thirupathiah, S., Borisenko, S.V., Ignatov, A., Kolchmeyer, D., Blumberg, G. and Paglione, J. Isotropic multi-gap superconductivity in $BaFe_{1.9}Pt_{0.1}As_2$ from thermal transport and spectroscopic measurements. Superconductor Science and Technology, 28, 014004 (2015). Invited submission for focus issue on Multicomponent Superconductivity. [4] Thorsmolle, V. K., Khodas, M., Yin, Z. P., Zhang, C., Carr, S. V., Dai, P., and Blumberg, G. (2014) Critical Charge Fluctuations in Iron Pnictide Superconductors. Research article under evaluation with Science. ArXiv e-prints <http://arxiv.org/abs/1410.6456>. [5] Zhang, W.-L., Richard, P., Ding, H., Sefat, A. S., Gillett, J., Sebastian, S. E., Khodas, M., and Blumberg, G. (2014) On the origin of the electronic anisotropy in iron pnictide superconductors. Under evaluation with Phys. Rev. Lett. ArXiv e-prints <http://arxiv.org/abs/1410.6452>.

EARLY CAREER: Spin Wave Interactions in Metallic Ferromagnets

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Funding: \$150,000 (2014)

PROGRAM SCOPE

Spin waves in ferromagnetic materials play a key role in a range of intriguing phenomena. Recent work shows that spin dynamics measurements can provide a means to quantify spin Hall effects and, conversely, that spin accumulation effects can be used to influence propagating spin waves. At the same time, the macroscopic length scales associated with thermally-driven spin phenomena in magnetic materials have raised new questions regarding the coupling between magnons, phonons, and spin accumulation effects. The goal of this project is to investigate two main directions related to spin dynamics in ferromagnets, namely the interactions between spin currents and propagating spin waves and the role of magnons and phonons in thermally-driven spin effects. Brillouin light scattering, a technique that is sensitive to both spin wave excitations or magnons and phonons, will be used to explore the fundamental nature of these effects.

FY 2014 HIGHLIGHTS

Highlights from FY 2014 include the observation of directly-excited backward volume (BV) spin waves in patterned ferromagnetic nanowires over a range of magnetic fields, including zero field, and investigations of the effect of thermal gradient on spin waves propagation using Brillouin light scattering (BLS). Previous experimental work on spin wave propagation in ferromagnetic nanowires has mainly been performed in the magnetostatic surface wave or Damon-Eshbach (DE) configuration where a static magnetic field is applied in-plane, perpendicular to the wire since spin waves can be excited relatively easily in this configuration. The less studied BV configuration where the magnetization is along the wire is, however, also of interest because spin waves can propagate even in the absence of an external magnetic field in this geometry, which is attractive for applications. Micro-BLS measurements show that although the intensities of the spin waves in the BV geometry were an order of magnitude lower than those observed in the DE configuration, BV spin waves were detectable at a range of magnetic fields including zero. The results agree well with dispersion calculations for propagating BV spin waves that include quantization effects due to the finite dimensions of the nanowire. Although many experiments have been done in the BV geometry in low-loss yttrium iron garnet (YIG), few have been done in nanowires hence these results are an important step towards nanoscale spin wave devices. BLS was also used to study how spin waves are affected by the presence of a thermal gradient, this time in a YIG thin film so that the effects could be studied over longer length scales (millimeters). The BLS data reveal subtle changes in the spectra at low frequencies that become more substantial at higher frequencies. Furthermore, significant changes in the amplitude were detected for a spin wave pulse that travels towards a heated area, an effect that may be useful for applications.

Cold Exciton Gases in Semiconductor Heterostructures

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Funding: \$180,000 (2014)

PROGRAM SCOPE

An indirect exciton is a bound pair of an electron and a hole confined in spatially separated layers. Long lifetimes of indirect excitons allow them to cool down to low temperatures below the temperature of quantum degeneracy. This gives an opportunity to realize cold excitons. Due to their long lifetimes, indirect excitons can travel over large distances before recombination. The spatial separation between an electron and a hole and the suppression of exciton scattering in a coherent exciton gas result to the suppression of spin relaxation facilitating long-range spin currents. Indirect excitons are dipoles, and their energy can be controlled by voltage. This gives an opportunity to create potential landscapes for indirect excitons. The goal of this project is to explore these properties of indirect excitons to study cold excitons in periodic potential landscapes and to study spin-related phenomena in cold exciton gases. We will study exciton transport in periodic potential landscapes. We will also develop stirring potentials for excitons based on the recently developed moving lattices for excitons. We will also study spin transport of excitons. Exciton transport, spin transport, and coherence will be measured by imaging, polarization-resolved imaging, and shift-interferometry imaging.

FY 2014 HIGHLIGHTS

We demonstrated experimental proof of principle for a stirring potential for indirect excitons. The azimuthal wavelength of this stirring potential is set by the electrode periodicity, the amplitude is controlled by the applied AC voltage, and the angular velocity is controlled by the AC frequency. We proposed the application of nonlinear optics for studies of spatially indirect excitons, demonstrated that despite their vanishing oscillator strength, indirect excitons can strongly contribute to the photoinduced reflectivity and Kerr rotation, and found in pump-probe measurements that the spin relaxation time of indirect excitons exceeds one of direct excitons by two orders of magnitude. We observed spin currents and polarization patterns in optically created indirect excitons.

Quantum Materials at the Nanoscale

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Funding: \$60,000 (2014)

PROGRAM SCOPE

One of the overarching goals of this program is to study collective effects and emergent phenomena in strongly correlated bulk crystals and films by quantum mechanically 'tuning' these systems with pressure, magnetic field, doping, and epitaxial strain. Among the specific goals of this project are to clarify the origins of, and ultimately control, collective phenomena (e.g., exotic phases, multiferroic behavior, etc.) in crystals and films such as magnetically frustrated spinels, orbital-ordering compounds (e.g., KCuF_3 , Ca_2RuO_4), charge density wave materials (e.g., ZrTe_3 , TiSe_2 , and TaS_2), and the superconducting cuprate $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$. A key tool for achieving these goals rests in our unique capability to perform inelastic light (Raman) scattering spectroscopy of spin and lattice excitations while tuning the sample environment as simultaneous functions of temperature-, magnetic-field-, and pressure. With this unique combination of environmental tuning capabilities, we have the opportunity to create and study novel states of matter in as-yet-unexplored phase regimes. The potential transformative impact of this approach is that it can provide new microscopic details regarding the evolution of exotic phase behavior and phenomena through pressure- and field-tuned transitions in extreme phase regimes of strongly coupled materials that are not accessible with other spectroscopic techniques. The current project supported 2 graduate students (1/2 year each) during fiscal year 2014.

FY 2014 HIGHLIGHTS

Superconductivity evolves as functions of pressure or doping from charge-ordered phases in a variety of strongly correlated systems, suggesting that there may be universal characteristics associated with the competition between superconductivity and charge order in these materials. A particularly interesting group of materials in which phase competition between charge and superconducting order appears to be important is charge-density-wave (CDW) materials that can be tuned to superconductor phases with either pressure or intercalation. These systems offer the opportunity to explore the competition between charge-order and superconductivity, and particularly the structural changes that enable the emergence of superconductivity as the CDW state collapses with increasing pressure or intercalation. During this past fiscal year, we have used variable-temperature and variable-pressure inelastic light (Raman) scattering to investigate the microscopic details underlying the pressure induced phases of the CDW system, ZrTe_3 . In this research, we showed that certain phonon bands of ZrTe_3 undergo dramatic linewidth reductions near T_{CDW} , indicating that these phonons couple strongly to the electronic degrees of freedom associated with the CDW. The same phonon bands, which represent internal vibrations of the ZrTe_3 prismatic chains, are suppressed at pressures above 10 kbar. This indicates a pressure-induced loss of long-range order within the chains, specifically amongst the intra-chain Zr-Te bonds. We also find structural evidence for pressure-induced dimensional crossover in ZrTe_3 . These results suggest a distinct structural mechanism for the observed suppression of CDW formation above 20 kbar and provide insights into the origin of pressure-induced superconductivity in ZrTe_3 .

Novel Sample Structures and Probing Techniques of Exotic States in the 2nd Landau Level

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Funding:	\$408,000 (2014-2016)

PROGRAM SCOPE

The two-dimensional electron gas is home to a wealth of unusual phases arising from the interplay of reduced dimensionality and strong electron-electron interactions. Recently it was suggested that this system may support unusual ground states which harbor exotic particles which special topological properties. Several of these unusual states develop in high purity AlGaAs/GaAs heterostructures in the region of the phase space called the second Landau level. Examples are the fractional quantum Hall states at the quantum numbers $5/2$ and $12/5$. We pursue a synergistic combination of growth and measurement techniques in order to gain new insight into the nature of the unusual fractional quantum Hall states of the second Landau level. Since the unusual fractional quantum Hall states are fragile, they are most often studied in a narrow range of samples parameters which maximize their strength. The goal of our project is to gain information on these states over an extended range of sample parameters. For this purpose we grow specially tailored AlGaAs/GaAs heterostructures with varying quantum well thickness, density, and disorder level and we employ ultra-low temperature transport and high pressure investigative tools.

FY 2014 HIGHLIGHTS

(1) We have upgraded our MBE system with a new auxiliary source cleaning chamber. As a result we have recently achieved $30 \text{ million cm}^2/\text{Vs}$ mobility. (2) We completed the growth and characterization of a sequence of samples with varying alloy disorder in the channel. We found that the fractional state at $5/2$ survives to much lower electron mobilities than previously thought. Conclusion: Alloy disorder is not particularly detrimental to the formation of the fractional quantum Hall states. These measurements suggest ways of improving the quality of these samples by eliminating impurities with long range scattering potential which are most likely to have the strongest deleterious impact on these states. (3) We have successfully fabricated low-leakage in-situ backgated 2DEGs for density dependent study of the fractional quantum Hall effect (FQHE) in the 2^{nd} Landau level. Ongoing work includes incorporation of nanostructures on to these density-tunable structures. (4) We explored the growth of samples with added charge disorder. Ongoing energy gap measurements have provided feedback on the amount of charge disorder to be added in future growth campaigns. (5) We explored the fractional quantum Hall states of the second Landau level at hydrostatic pressures of the order of 10 kbar. We have observed a novel phase transition in the state at quantum number $5/2$ that we currently study in detail. (6) We have collaborated with the PIs Rokhinson and Lyanda-Geller on strain measurements of the reentrant insulating states believed to be exotic electronic solids. Results: We found evidence of novel topological excitations which do not exist in other types of electron solids.

Spin Dependent Transport in Metallic Nanoparticles

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Funding: \$130,000 (2014)

PROGRAM SCOPE

The directional instability of magnetization in nanometer-scale ferromagnets arises due to the irreversible coupling of a magnetic sample to its environment, which induces spin randomization. This effectively quenches the ferromagnetic state and its key signature of magnetic hysteresis. The crossover from stable hysteresis to spin randomization is particularly pertinent as the length scale is reduced, and is well understood in the case of thermal equilibrium. However, in the case of a perturbed, non-equilibrium ferromagnet, this crossover is more difficult to address. All of the prior works reinforce the notion that magnetism on the length scales of about 1-3nm is significantly influenced by the local environment. In this project we investigate the mechanism of coupling between a nanomagnet and its environment out of equilibrium, which leads to magnetization randomization. We find that a single Ni particle $\approx 2.7\text{nm}$ in diameter, embedded within a double-barrier tunneling device, will only exhibit magnetic hysteresis under narrowly defined circumstances at low temperatures. In particular, the degree of magnetic stability depends on the value of the source bias. Over a finite energy bandwidth, magnetic hysteresis is only weakly dependent on voltage. Toward the edge of this bandwidth, however, magnetic hysteresis quickly diminishes.

FY 2014 HIGHLIGHTS

Magnetic properties of single Ni, Co, and Fe particles 2-3nm in diameter are studied by single electron tunneling spectroscopy at temperature of 15mK and higher. It is found that the Ni particles lie at the threshold of stable ferromagnetic order, in a sense that a fraction of the Ni nanoparticles exhibits no magnetic hysteresis at all, while the remaining fraction has magnetic hysteresis that quickly vanishes as the temperature increases above 2K. In comparison, all Fe and Co nanoparticles are found to exhibit magnetic hysteresis at 4.2K, while single magnetic molecules studied by different groups, do not display any magnetic hysteresis under condition of electron tunneling at low temperatures. Thus, Ni nanoparticles fall into the critical range where magnetism is extinguished by electron transport. This regime permits investigation of the physical mechanism for the destruction of stable ferromagnetic order in magnetic nanostructures under condition of electron transport. That mechanism is revealed by our experiments and theoretical simulations. We find that the bias voltage serves as an effective energy limiter to the magnetic excitation energy of the particle. The spin-orbit scattering rate emerges as the characteristic frequency that governs the stability of magnetization as a function of voltage bias.

Disorder and Topological Defects in Magnetically Frustrated Single Crystals and Thin-Film Metamaterials

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Funding: \$73,960 (2014)

PROGRAM SCOPE

A fundamental investigation of the effects of controlled disorder and reduced symmetry on patterned thin-film metamaterials is focused on a new class of artificial magnetic quasicrystals that exhibit geometric frustration and complex spin ice behavior. The signature long-range order without periodic

translational symmetry of quasicrystal tilings places them in a unique niche between periodic crystals and amorphous materials. Bulk magnetic quasicrystals exhibit striking physical properties and frustration, but they are difficult to grow and characterize, and are known to adopt spin-glass, rather than long-range magnetic order. The program therefore takes advantage of recent advances permitting nanofabrication of ferromagnetic (FM) thin films into “artificial quasicrystals” whose spin wave excitations and reversal can be systematically controlled via tiling design. The program will pursue spin wave localization due to controlled lattice disorder, and finite-size scaling behavior of static and dynamic physical observables in patterned films having variable topology, size and order. In-house ferromagnetic resonance, static magnetization and numerical simulations characterize spin wave excitations, frustration and possible phase transitions among spin ice phases. The unique temporal coherence and phase sensitivity of X-ray photon coherent scattering (XPCS) has enabled the first studies of magnetic relaxation and nonequilibrium dynamics of spin ices as a function of temperature and magnetic field over a broad interval of time scales (10^{-3} to 10^3 s). Direct nanoscale imaging techniques (coherent X-ray scattering, magnetic force microscopy (MFM) and scanning electron microscopy with polarization analysis (SEMPA)) characterize equilibrium magnetic textures and defects of spin ices of various topologies for comparison to dynamical data and numerical simulations.

FY 2014 HIGHLIGHTS

We have extended a first study of the effects of quasicrystal symmetry on cooperative interactions, frustrated dynamics and equilibrium ground state of Penrose P2 tilings, whose asymmetric pattern vertices strongly affect magnetic reversal and spin wave (SW) spectra [1]. We have observed first evidence of long-range magnetic order and “complex spin ice behavior” in direct SEMPA imaging of artificial P2 tilings [2]. Our first fabrication of aperiodic, long-range-ordered lattices based on Fibonacci distortions of periodic Bravais lattices allow us to investigate the effects of continuously variable aperiodicity on magnetic reversal, dynamics and spin ice behavior [3]. Recent XPCS experiments [4] have shown modest applied magnetic fields can control transfer of orbital angular momentum to a soft X-ray vortex beam resonantly scattered from suitably designed artificial spin ices, which promises to enable novel photonic technologies. [1] “Non-stochastic switching and emergence of magnetic vortices in artificial quasicrystal spin ice”, V. S. Bhat, B. Farmer, N. Smith, E. Teipel, J. Woods, J. Sklenar, J. B. Ketterson, J. T. Hastings and L. E. De Long, *Physica C* 503, 170-174 (2014). [2] “Direct Imaging of Complex Spin Ice Behavior and Ordered Sublattices in Artificial Ferromagnetic Quasicrystals”, V. S. Bhat, Andrew Balk, B. Farmer, E. Teipel, N. Smith, J. Unguris, J. T. Hastings and L. E. De Long, submitted *Physical Review Letters* (December, 2014). [3] “Magnetic Response of Aperiodic Wire Networks Based on Fibonacci Distortions of Square Antidot Lattices”, B. Farmer, V. S. Bhat, J. Sklenar, E. Teipel, J. Woods, J. B. Ketterson, J. T. Hastings and L. E. De Long, to be published in *J. Appl. Phys.* (2014). [4] “Creation of x-ray vortex beams using an artificial spin ice structure”, S. K. Mishra, J. C. T. Lee, V. S. Bhat, X. Shi, D. H. Parks, B. Farmer, L. E. De Long, I. McNulty, S. D. Kevan and S. Roy, submitted as a Letter to *Nature Photonics* (August, 2014).

Dynamics of Electronic Interaction in Superconductors and Related Materials

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Funding: \$340,000 (2014-2015)

PROGRAM SCOPE

We will perform experimental ARPES studies of the dynamics of electronic interactions in high temperature cuprate superconductors and related materials, especially electron and hole-doped $J=1/2$ Mott insulating iridates. For the ARPES studies on the cuprates we will utilize the new TDoS (Tomographic Density of States) method that we introduced previously, which integrates out most of the unknowns of the ARPES lineshape and for the first time allows quantitative extractions of superconducting gaps Δ and pair-breaking interactions Γ . In contrast to the case of BCS superconductivity, our TDoS results show that the pair-breaking Γ is large and strongly temperature dependent, and appears to play a critical role in cuprates – for example conspiring with the gap to set the T_c . We will extend our TDoS efforts here, among other things working to understand the details and origin of the unusually rapid growth of the pair-breaking scattering rate with temperature. We will study other strongly correlated electronic oxides, especially the new electron and hole-doped $J=1/2$ Mott insulating iridates, which show many similar phenomena as the cuprates. These include Fermi arcs and pseudogaps, with the combination of data giving new insights into these phenomena.

FY 2014 HIGHLIGHTS

We have accomplishments in the advancement of the technique of ARPES as well as in its application to a few different materials. Here we focus on the work that was published in this year. A) We published a paper in Review of Scientific Instruments on the nonlinearity of counting rates present in all modern commercial multichannel analog electron detectors. We show the effects that this commonly-ignored effect has on the spectra, as well as a new highly-efficient method to remove its effect from the data. This greatly increases the quantitative accuracy of modern ARPES data. B) We published a paper on the metallic pyrochlore iridate $\text{Bi}_2\text{Ir}_2\text{O}_7$, which was the first experimental electronic structure measurement of a pyrochlore iridate. Our work showed decent agreement with our companion density functional calculations, setting the stage for measurements and comparisons with other pyrochlore iridates, especially non-metallic ones that have stronger correlation effects and more exotic physics. C) We published a joint theory/experiment paper on a tight-binding model of bilayered manganese oxides. A key aspect of this work is that it allows a simple and accurate way to obtain the electronic structure as a function of the relative canting angle of the spins between the sheets in a manganese-oxide bilayer – something that has so far not been possible by any standard technique.

Infrared Hall Effect in Correlated Electronic Materials

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Funding: \$145,093 (2014)

PROGRAM SCOPE

The research program has two thrusts: IR Hall Effect in cuprate superconductors and the THz magneto-optics of topological semiconductors. These two classes of materials have had a profound impact on the condensed matter community. The sensitive infrared Hall spectroscopy techniques developed by the PI

at the University of Maryland are being used to investigate materials in these two classes. In the cuprates, the extent to which Fermi liquid theory provides an adequate description of transport and infrared properties is being critically examined across the pseudogap range of the doping phase diagram of p-type cuprate superconductors. The data from our spectroscopic infrared magneto-transport measurements are being compared with the data acquired from Angular Resolved Photoemission Spectroscopy and other experiments such as DC transport and neutron scattering in order to critically test theories. The goal of this effort is an elucidation of the physics of the pseudogap phase of cuprate superconductors. In the topological insulators our magneto-optical techniques provide a powerful means to characterize the Dirac dispersion relation through cyclotron resonance and Faraday rotation. Also while much of the initial work on topological insulators and 3D Dirac semimetals involved surface sensitive probes like ARPES and STM, such techniques are not appropriate for probing bulk properties or buried interface states that are necessary in applications. Novel THz magneto-optical effects have been predicted. In particular, broken time reversal ground states can be detected and effectively probed using Kerr rotation. We are searching for this effect in InSb/GaSb quantum wells which is predicted to have excitonic insulator ground states with broken time reversal. In addition novel surface states exhibiting Fermi arcs have been predicted to exist in 3D Weyl semimetals but have not yet confirmed. Our experiments are designed to investigate these novel predictions.

FY 2014 HIGHLIGHTS

During the 2014 funding year of this award the main effort has been focused on the installation of a Helium recovery and liquefaction system and the renovation of our magneto-optical measurement system for improved stability and to allow higher data throughput. We have also worked on the acquisition and preparation of samples for our magneto-optical measurements on cuprate superconductors and topological insulators and their preliminary optical characterization. The new samples include Bi(2201) single crystal samples provided by Andrea Damescelli, UBC, Canada. We have cleaved Bi(2201) to 100 nm thickness and approximately 100 microns diameter. In order to measure the Faraday rotation with greater precision we are also obtaining large area Bi(2201) films from Dr. Helene Raffy of Laboratoire de Physique des Solides, Universite & Paris Sud, Orsay, France. The second thrust of our fundamental research is on topological insulators with a focus on measuring the magneto-optical response of several candidate materials predicted to have 3D Weyl states. We have made zero field IR optical measurements on of $\text{Eu}_2\text{Ir}_2\text{O}_7$. These data have shown a linear frequency dependence of the optical conductivity in the IR as has been predicted for a 3D Weyl state system. This work is being prepared for publication. The samples for these experiments were provided by Satoru Nakatsuji of University of Tokyo. Our study of 3D Weyl state systems has also been expanded to include several newly discovered systems. They include Cd_2As_3 and Na_3Bi which have been observed to have a Dirac spectrum by ARPES. These materials are being provided by Robert Cava of Princeton University. We have observed the Pauli blocking interband edge for the Weyl bands in Cd_2As_3 . We have also begun work on InSb/GaSb quantum wells, a promising new topological insulator. These samples have been provided by Rui-Rui Du of Rice University.

Microwave Spectroscopy of Electron Solids: Fractional Quantum Hall Effect and Controlled Disorder

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

Electron solids related to the Wigner crystal figure importantly in the proposed work. Such solids are present in GaAs at the low Landau filling (ν) termination of the fractional quantum Hall (FQH) series, and within integer quantum Hall effect plateaus, though not exactly at integer ν . These solids are insulators due to pinning by disorder, and exhibit a striking resonance in their microwave or rf spectrum. The resonance is understood as a pinning mode, in which pieces of the solid oscillate within the disorder potential. Due to these resonances, broadband microwave spectroscopy is a natural way to study these phases, and is the tool used in this project. The current scope of the project involves both samples with controlled alloy disorder, and ultralow disorder wide quantum wells.

FY 2014 HIGHLIGHTS

We have published one paper and submitted one more on pinning modes of 2DES residing in $\text{Al}_x\text{Ga}_{1-x}\text{As}$, with $x < 1\%$, in which the Al provides controlled short range random disorder. We found the pinning mode of Wigner solid to be remarkably robust in the presence of this disorder. Near $\nu=1$, the pinning modes of disordered samples which are likely due to composite fermion Fermi surface effects. In addition, we have begun to pursue work on low disorder wide quantum wells, publishing one paper on a phase transition (likely involving spin and composite fermion vortex number) in the vicinity of $\nu=1$. We have submitted a paper on phase transitions found in the insulator that terminates the fractional quantum Hall series, in a regime where the 2DES is expected to form a bilayer solid. The work indicates that the bilayer 2DES produces phases that may have domains of liquid and bilayer solid, or of two bilayer solids of different crystal structure. Finally we have studied low magnetic field nonlinear response of 2DES to the combination large dc current and large microwave power, using a coaxially driven coplanar waveguide set up that is unique for studies of this type, and published a paper on that work.

Atomic Layer Controlled Growth of Artificially Engineered Pnictide Superlattices By Design

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Jointly funded by "Experimental Condensed Matter Physics" and "Synthesis and Processing Science"

PROGRAM SCOPE

Since the discovery of superconductivity in iron-based materials significant progress has been made in the fabrication of high quality bulk and epitaxial thin film materials to explore their intrinsic properties and evaluate novel device applications. The superconducting mechanism, structural transitions, magnetic behavior above and below T_c , interfacial phenomena, and critical current and flux-pinning behavior have all been recognized as critical to progress toward understanding the pnictides. Artificial layered pnictide superlattices with atomically sharp heterointerfaces offer unique opportunity towards tailoring superconducting properties and understanding the mechanisms of superconductivity by

creating model structures which do not exist in nature. Our main tasks are to create and control pnictide superlattices and heterointerfaces at the atomic level, to understand the relation between structure, magnetism and superconducting properties, and to design and grow novel pnictide superlattices tuned to take advantage of the superconducting structure/property relationships possible in this unique new superconductor. The thrusts of our proposed work are: (1) Atomic-layer-controlled growth of artificially engineered superlattices. (2) Designing interfacial superconductivity at pnictide and FeSe interfaces. (3) Investigation of interaction between superconductivity and magnetism by proximity effect (4) Understanding and control of flux-pinning mechanisms (5) Study of growth mechanisms of heteroepitaxial superlattices and artificial pinning centers. The proposed work investigates the basic physical processes of novel superconductivity, primarily by looking at its interaction with magnetism on a microscopic scale, and the role these play in the flux pinning process. We also extend these fundamental investigations to explore routes to interfacial superconductivity in these systems.

FY 2014 HIGHLIGHTS

We investigated the superconducting properties of single- and multilayer Co-doped BaFe₂As₂ (Co-Ba122) thin films grown on CaF₂ and (LaAlO₃)_{0.3}(Sr₂AlTaO₃)_{0.7} (LSAT) substrates. We confirmed the significant improvement of the critical temperature in the film on CaF₂ and we demonstrated that the multilayer deposition has no detrimental effect on T_c. We found that deposition on CaF₂ produces much cleaner films compared to films on LSAT, since on CaF₂ the substrate absorb oxygen preventing the formation of the high density of defects present in the LSAT case. The result of this oxygen reaction is that in the single layer on CaF₂ (CaF-S) the only visible defects are dislocations. Moreover, the different trend of angular dependence of critical current density in CaF-S at intermediate temperature suggests an increasing contribution of point defects with decreasing temperature. The multilayer film on CaF₂ (CaF-M), grown with insertion layers enriched in BaO, does have defects including short nanorods, round particles and flat particles similar in size but with a lower density to those in films on LSAT. Despite the different pinning mechanisms that affect the shape of the angular dependence of J_c, the single layers on both substrates roughly have similar J_c at the same reduced temperature. In contrast the multilayer deposition on CaF₂ is 2-3 times more effective in increasing J_c with respect to the corresponding single layer than in the LSAT case. This results in a record high pinning force (F_p) of 84 and 70 GN/m³ in Ba122 phases (H//ab and H//c, respectively), significantly larger than reported previous values in the Co-Ba122 phase and higher-T_c P-Ba122 phase. Applications interest is strengthened by their notably better in-field performance than in Nb₃Sn.

High-Bandwidth Scanning Hall Probe Imaging of Driven Vortices in Periodic Potentials

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Funding: \$49,247 (2014)

PROGRAM SCOPE

This project will use a novel technique, high-bandwidth scanning Hall probe microscopy, to study the local, real-time dynamical states of current-driven vortices in artificially structured periodic potentials. This technique extends the frequency response of Hall probe microscopy from the usual 10-100 Hz used

for imaging into the MHz range. Using this new technique, the dynamics of driven vortices can be probed with an unprecedented combination of temporal and spatial resolutions, allowing a wealth of new physics, inaccessible to other measurements, to be uncovered. A number of specific experimental systems will be explored. Vortices moving in periodic potentials have unique depinning signatures that can best be addressed by real-space imaging. Once vortices are moving, a variety of dynamical states are predicted, including simple channeled flow and several more complex disordered flows. There are also remarkable effects observed when vortices are driven, in addition to a dc current, a high-frequency ac current. Here, striking steps are found in the dc voltage as the dc driving current is increased. Another exciting recent discovery is the 'vortex ratchet,' in which vortices are driven by a symmetrical ac current in an asymmetrical background potential. This leads to an overall dc motion of the vortices, that is, the vortex motion is rectified. The real-space, dynamical nature of all of these systems are best explored by a high-bandwidth imaging technique. The proposed work will open entirely new avenues for exploration in vortex physics. Questions to be addressed include: How do vortices depin from a periodic potential? Once the vortices are in motion, what is the detailed nature of the moving states? How do the vortices respond to high-frequency driving forces? And how does vortex transport proceed when the potential has a built-in directional bias? And, most importantly, how do all these process depend on the degree of commensurability?

FY 2014 HIGHLIGHTS

During fiscal year 2014, we have completed development of the complex instrumentation and specialized samples required for the project. Specific instrumentation projects completed include the fabrication of a temperature-stabilized, low-vibration cryocooler, a scanning Hall probe microscope with its associated probes, and a combined evaporation/sputtering chamber used for growth of superconducting samples and Hall probe contacts. We have developed a novel technique for fabricating the specialized samples needed for the project. By sputtering superconducting films onto a substrate that has a periodic modulation in its thickness, we can create films with tailored periodic vortex potentials. These films can be grown to be highly symmetric, so that vortices move equally in either direction, or asymmetric, so that there are 'hard' and 'easy' directions for vortex motion. The results of transport measurements on these films will be reported soon, and imaging experiments are currently underway.

Symmetries, Interactions and Correlation Effects in Carbon Nanotubes

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Funding: \$150,000 (2014)

PROGRAM SCOPE

The PI's group has recently developed a unique platform for studying the effects of dissipation and interactions on quantum impurity systems, which is based on a carbon nanotube quantum dot with dissipative leads. Tunneling in the Ohmic dissipative environment is known to emulate tunneling in the Luttinger liquid – an archetypical example of an interacting one-dimensional electron system. We have first studied resonant tunneling (i.e. tunneling through an intermediate resonance) in this system, and

observed unitary resonances with vanishing width, predicted for the Luttinger liquid back in 1992 (Nature 2012). We have interpreted the observations in terms of a quantum critical behavior enabled by dissipation. One of the main topics of this project is to further develop the analogy between dissipative environment and the Luttinger liquid, and experimentally realize many “quantum impurity” models with Luttinger leads, for which a rich body of theoretical knowledge has been accumulated, but experimental results are scarce or nonexistent. Our work aims to enhance understanding of electronic interactions and dissipative phenomena in low-dimensional confined nanostructures, which naturally possess high degree of symmetry. Interactions and symmetries in confined systems are one of the fundamental topics in the modern condensed matter physics.

FY 2014 HIGHLIGHTS

We have investigated the exotic state of electronic matter obtained by fine-tuning the system exactly to the quantum critical point (QCP) that we observed earlier. We have reported on several transport scaling laws both near and far from equilibrium, including a non-Fermi-liquid quasi-linear scattering rate at the QCP, interpreted in terms of a Majorana mode localized at the resonant level (Nature Physics 2013). We have further investigated the QCP in collaboration with theoreticians. Specifically, we considered the non-equilibrium effects (PRB 2013) and the role of dissipative gate in tuning the properties of the QCP (PRB 2014). We have also conducted two additional experimental projects. We observed a “bottleneck” in thermal transport between electrons and the substrate in graphene at mK temperatures, allowing for the electrons to be significantly hotter relative to the phonons. This effect may have important applications in ultra-sensitive cryogenic graphene-based detectors (PRL 2013). In collaboration with chemistry colleagues, we developed an alternative catalyst for growing carbon nanotubes that results in tighter control of the nanotube diameter (ACS Nano 2014).

Tunneling and Transport in Nanowires

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Funding:	\$225,000 (2014-2015)

PROGRAM SCOPE

The goal of this program is to obtain a fundamental understanding of phenomena that might be relevant to the performance of devices and circuits at the limit of the smallest realizable feature sizes. The approach is to study nanowires prepared using top-down physical, rather than bottom-up chemical or biological techniques. When the transverse dimensions are smaller than the inelastic scattering, phase coherence, or superconducting coherence lengths, the wires are quasi-1D. Truly 1D wires are those for which the transverse dimensions are smaller than the Fermi wavelength. For such wires Landau Fermi liquid theory should be replaced by Tomonaga-Luttinger Liquid (TLL) theory. We propose to carry out two classes of experiments on nanowires prepared using electron beam lithography (EBL). The first involves studies of quasi-1D superconductors. We are investigating the mechanism for the restoration of superconductivity by small magnetic fields of nanowires driven resistive by current. This is a phenomenon that we discovered, and have found an explanation involving the counterintuitive idea that superconductivity and dissipation can coexist in certain out-of-equilibrium situations. We are also

studying superconductor-insulator transitions controlled by dissipation. Understanding these transitions will advance our knowledge of quantum phase transitions in reduced dimensions. The level of dissipation will be controlled by changing the conductivity of a two-dimensional electron gas in close proximity to the nanowire. The second class of experiments is directed at exploring the TLL regime of a 1D wire prepared from a low carrier density material, electrostatically doped strontium titanate (STO). We will employ EBL to form a surface mask, and will use an ionic liquid to induce charge in an exposed line of STO. If the lines can be made sufficiently narrow, then when lightly doped, they may exhibit TLL behavior.

FY 2014 HIGHLIGHTS

There has been major progress in the investigations of the properties of superconducting nanowires and of ionic-liquid-gated nanometer scale channels of strontium titanate (STO). As to superconducting nanowires, a paper was published in Nature Physics entitled, "Dissipative superconducting state of non-equilibrium nanowires." It is generally thought that superconducting order is incompatible with dissipation. The one exception is vortex flow, which takes place in sufficiently high magnetic fields. We have observed dissipative superconductivity in far more basic configurations: superconducting nanowires with superconducting leads. We have found that dissipative normal current may flow in the presence of superconducting order throughout the wire. We attribute the phenomenon to the formation of a non-equilibrium state, where superconductivity coexists with dissipation, mediated by Andreev quasiparticles. The effect is an example of a controllable non-equilibrium state of a quantum liquid. These findings suggest that nanowires can serve as a platform to investigate conceptual problems of out-of-equilibrium quantum systems. The I-V characteristics of ionic-liquid-gated nanometer scale channels of STO have been found to exhibit a voltage threshold for conduction and a power law behavior. The temperature dependence of the threshold voltage appears to be related to the inverse of the temperature dependent dielectric constant of STO in qualitative agreement with a model of charge density wave depinning. These observations, when taken together, are evidence that a charge density wave, which can be de-pinned by strong electric fields, has been induced. This work has been written up and a manuscript entitled, "Charge Density Wave Behavior of Ionic Liquid Gated Strontium Titanate Nanowires," is under review by Physical Review Letters. Whether these findings preclude the study of Tomonaga-Luttinger liquid behavior of these channels is an open question.

Colloidal Quantum Dot Films, Transport and Magneto-Transport

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Funding: \$95,862 (2014)

PROGRAM SCOPE

The program is to investigate the conductivity and magnetism in solids of colloidal quantum dots. In the foreseeable future, 3D nanostructured materials are a likely source of novel properties, and the colloidal quantum dots provide an initial step in that direction. Starting with colloidal quantum dots of targeted materials, synthesized by chemical means, the program aims to achieve strong enough coupling between these quantum dots, without losing their quantized level structure, in order to obtain useful

conductivity. The applications already explored include photodetection, photovoltaics and light emitting devices. The basic research program investigates the conductivity as a function of the coupling between the particles, the temperature, the bias and the carrier density. The program distinguishes itself from others by carefully identifying the Fermi level position in relation to the quantum dot states, such that transport is taking place through the quantum dots rather than through an unknown density of states in the surrounding matrix or interfaces. Transport measurements are jointly carried out with optical measurements. The magnetic properties of the quantum dots are primarily addressed by considering unpaired electrons and magnetic impurities. In quantum dots, such unpaired electrons are expected to also lead to magnetic effects which could be switchable by changing the carrier density. In the regime of weak coupling between colloidal quantum dots, there is a spin blockade effect which can give positive or negative magnetoresistance (MR). In the presence of magnetic impurities inserted in the quantum dots and unpaired delocalized electron, there is the possibility of forming magnetic polarons with a large paramagnetic moment. This grant investigates the magneto resistance of a number of colloidal quantum dot systems with and without magnetic impurities with the aim to discover a new approach to materials with coupled electric, magnetic and optical properties.

FY 2014 HIGHLIGHTS

We reported the first detailed study of 1/f noise in nanocrystal solids. We initially expected that 1/f noise could be reduced by film processing, by the choice of the materials comprising the nanocrystals, and by the choice of the matrix. We did find that cracks in films increased the 1/f noise. However, for good films of all the different materials studied, we found a “universal” 1/f noise floor, with a noise scaling as the number of nanocrystals in the system, i.e. extensive as for bulk systems, and approximately proportional to the interdot conductance, irrespective of the materials. We qualitatively concluded that the noise is an intrinsic effect of the granularity in conduction, where charges moving in weakly connected part of the network modify the transport in the higher conductivity regions.

Linear and Nonlinear Optical Properties of Metal Nanocomposite Materials

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Funding: \$350,826 (2014-2015)

PROGRAM SCOPE

The central theme of this project is nonlinear and ultrafast optics in metal nanoparticle composites, including metamaterials, exciton-plasmon coupling and plasmonic effects in metal-insulator transitions. For FY 2014, we focused on (1) ultrafast electron dynamics in metamaterials, including ultrafast THz microscopy of the insulator-to-metal transition in vanadium dioxide nanoparticles, plasmon-driven electron injection to promote phase transitions in vanadium dioxide and second-harmonic generation in nanostructures without inversion symmetry; and (2) dimensional and structural effects in plasmonic coupling, including exciton-plasmon coupling in zinc-oxide nanowires, in structures that incorporate two-dimensional atomic crystals and tunable plasmon-induced transparency heterostructures incorporating phase-changing vanadium dioxide. Aided by finite-difference time-domain and finite-element calculations, we design and fabricate heterostructures in which we can excite electrons and

quasiparticles (e.g., excitons, phonons, plasmons) and map the material response at femtosecond time and nanometer length scales. We employ nanofabrication tools (dual-layer electron-beam lithography, exfoliation of metal dichalcogenides, focused ion-beam nanomachining) and materials synthesis techniques (e-beam evaporation, vapor-solid nanowire/nanocrystal synthesis) developed during this project period to create novel heterostructures designed to elicit specific kinetic and dynamical responses. The complex phenomenology of these structures is studied using coherent, time-resolved second- and third-order optical spectroscopies, along with confocal and scanning-probe microscopies. We expect the proposed research projects to have significant impact on (1) optical physics in active and nonlinear metamaterials; and (2) ultrafast dynamics in heterostructures designed to elucidate the interactions of plasmons with material degrees of freedom.

FY 2014 HIGHLIGHTS

We measured the second-harmonic generation (SHG) efficiency of Archimedean nanospirals and used ultrafast, two-photon photoelectron microscopy to show that the region of strong excitation was at the focus of the nanospiral as seen in finite-difference, time-domain simulations. Arrays of 4π nanospirals were fabricated in square arrays by electron-beam lithography. Mode-locked pulses from a Ti:sapphire oscillator were passed through a spatial light modulator to create transform-limited pulses of 15 fs duration, at a pulse-repetition rate of 90 MHz. The efficiency of second-harmonic generation in this experiment is much larger than that reported for single gold nanocups or multiresonant antennas. Zinc oxide nanowires are a versatile workbench for studying optical emission and exciton dynamics in the near UV and visible. By depositing a variable thickness MgO shell on the ZnO nanowires and decorating the core-shell nanowires with Ag nanoparticles, the ZnO band-edge emission was strongly enhanced at specific thicknesses of the MgO shell, due to resonant optical-cavity effects. Moreover, the emission rate was further enhanced by the Ag nanoparticles, especially at higher spatial modes corresponding to thicker MgO shells; the larger spatial extent of the higher-order cavity modes results in an enhanced radiative emission rate. To better understand exciton-plasmon interactions we employed scanning transmission electron microscopy (STEM), cathodoluminescence (CL) and electron energy-loss spectroscopy (EELS), to achieve high resolution imaging with EELS while simultaneously detecting optical excitations and radiative decays. We used CL imaging to visualize ZnO emission in the presence of Ag nanoparticles. The locations in the ZnO with the highest emission correspond to strong plasmonic emission in the nanoparticles. Further, we can use the complementary nature of EELS and CL to discern the strength, localization and nature of plasmon modes on a single nano particle.

Antiferromagnetism and Superconductivity

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Funding: \$495,000 (2014-2016)

PROGRAM SCOPE

There is a growing impact of technological benefits to our society from basic research on superconductivity. Achieving high electrical current density in a magnetic field is a critical component of this progress. Our research program on Antiferromagnetism and Superconductivity exploits the power

of nuclear magnetic resonance (NMR) to investigate the magnetic and electric fields in superconductors on an atomic scale. Limitations in current density can be related to the dynamics of these vortices and the electronic structure in the vortex core for which NMR is an ideal probe. Using high magnetic fields at the National High Magnetic Field Laboratory and at Northwestern University we explore the electronic structure in the normal and vortex superconducting states of superconductors including Bi2212, Hg1201, and NaFeAs. For the heavy fermion compound UPt₃ we use national neutron scattering facilities to measure the vortex structure and magnetic spin susceptibility. With our collaborators we perform inelastic neutron scattering, tunneling spectroscopy, electrical transport, and optical Kerr rotation experiments. We grow and characterize the highest quality of UPt₃ single crystals and use these materials to define the order parameter symmetry and nodal gap structures in UPt₃, and the coupling of its magnetism to superconductivity. This is an unconventional superconductor that can be grown in our laboratory to unique levels of purity in single crystal form. It may be one of the best choices for understanding spontaneously broken symmetry in superconductors in the presence of competing interactions, such as is the case for magnetism.

FY 2014 HIGHLIGHTS

“The impact of helium shortages on basic research”, W.P. Halperin, *Nature Physics* 10, 467 (2014). “Observation of broken time-reversal symmetry in the heavy-fermion superconductor UPt₃”, E. R. Schemm, W. J. Gannon, C. Wishne, W. P. Halperin, Aharon Kapitulnik, *Science* 345, 190 (2014). “Absence of Static Current-Loop Magnetism at the Apical Oxygen Site in HgBa₂CuO₄+δ from NMR”, A.M. Mounce, Sangwon Oh, Jeongseop A. Lee, W.P. Halperin, A.P. Reyes, P.L. Kuhns, M.K. Chan, C. Dorow, L. Ji, D. Xia, X. Zhao, M. Greven, *Phys. Rev. Lett.* 111, 187003 (2013). “Microscopic coexistence of a two-component incommensurate spin density wave with superconductivity in underdoped NaFe_{0.983}Co_{0.017}As”, S. Oh, A.M. Mounce, J.A. Lee, W.P. Halperin, C.L. Zhang, S. Carr, P. Dai, A.P. Reyes, P.L. Kuhns, *Phys. Rev. B* 88, 134518 (2013).

Spin-Coherent Transport Under Strong Spin-Orbit Interaction

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Funding: \$330,000 (2014-2016)

PROGRAM SCOPE

The project acquires fundamental insight in spin-dependent quantum coherent phenomena arising from spin-orbit interaction, via experiments on semiconductor heterostructures and thin film semimetals patterned into mesoscopic and nanoscale geometries. The experiments are conducted by low-temperature electronic magnetotransport in nanoscale structures of length scales similar to the quantum phase- and spin-coherence lengths and the carrier mean free path of the materials used. Understanding of coherent spin-dependent electronic processes is obtained by the emphasis on quantum and spin coherence. Spin-orbit interaction in the solid-state can provide an avenue for spin operations in quantum information processing and for the creation of new quantum states of matter. The subject is of fundamental interest but also of long-term applied interest in magnetoelectronic and spintronics devices. In two-dimensional electron systems in quantum wells of the narrow-bandgap

semiconductors InAs and InGaAs the objectives include the measurement and characterization of quantum states arising from the Aharonov-Casher quantum-mechanical phase and its associated effective gauge field. The Aharonov-Casher phase is the electromagnetic dual of the Aharonov-Bohm phase, obtained by exchanging the magnetic fields and electric charges in the Aharonov-Bohm phase by electric fields and magnetic moments (spin). The objectives comprise studying an effective dual to the integer quantum Hall effect arising from the Aharonov-Casher effective gauge field. Objectives also include quantum electronic transport at the mesoscopic scale on the semimetal bismuth in thin film form, and particularly on its strongly spin-orbit coupled surface states. Using bismuth structures on the scale of the quantum phase- and spin-coherence lengths, the effects of the strong spin-orbit interaction on electronic properties and quantum states are elucidated.

FY 2014 HIGHLIGHTS

In InGaAs/InAlAs heterostructures, the dependence of quantum phase coherence on excitation current and temperature was studied using mesoscopic single-ring interferometers, using low-temperature Aharonov-Bohm oscillations in the magnetoresistance of individual rings. The Thouless energy was observed to be the relevant measure of excitation energies. An amplitude modulation was concluded to have its origin in the effect of the local magnetic flux through the interferometer arms (J. Phys.: Cond. Mat. 25, 435301 (2013)). Measurements of ring-array interferometers in Sagnac mode, where time reversal symmetry is broken by the local magnetic flux, show that the local magnetic flux in this case acts to limit quantum phase coherence. The spin coherence length was measured in InAs mesoscopic wires, where it was found that diffusive boundary scattering affects this length via the diffusion coefficient (Phys. Rev. B 88, 205407 (2013)). The spin coherence length is otherwise increased in narrow wires, interpreted as resulting from the duality between Aharonov-Casher and Aharonov-Bohm quantum phases. The observations about spin coherence lengths were extended to InSb and bismuth wires and an interpretation of results proposed (Proc. SPIE 9167, 91670-D1 (2014)). On InAs electron accumulation layers, the effect of rare-earth ions on the surface was measured using antilocalization (Chin. Sci. Bull. 59(2), 133 (2014)). The results show that antilocalization measurements can be used to study the interactions between surface species and local magnetic moments. Spin-flip rates were found to be affected by transitions between closely spaced energy levels of the surface species, and spin-orbit interaction to be modifiable by surface species. In InGaAs/InAlAs heterostructures, the effects on spin-flip rate and spin-orbit interaction due to nanolithographic ferromagnetic CoFe pillars was measured (Sol. State Comm. 177, 36 (2014)).

Charge and Energy Transfer in Molecular Superconductors and Molecular Machines

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Funding: \$137,886 (2014)

PROGRAM SCOPE

This project is to investigate charge and energy transfer processes at the ultimate atomic scale as well as novel physical phenomena associated with two nascent molecular systems; nanoscale molecular superconductors, and molecular motors on metallic surfaces. The experiments will be performed by

using scanning tunneling microscopy, tunneling spectroscopy, and atomic and molecular manipulation at low temperatures in an ultrahigh vacuum environment. This project includes both conventional and innovative experimental components, and the achievements of this project will not only enhance our understanding of charge and energy transfer processes at the atomic/molecular regime but also will impact a large area of science and engineering disciplines in general.

FY 2014 HIGHLIGHTS

(1) Adding Communication to Molecular Rotors: One of the goals of nanotechnology is to assemble billions of nanomachines packed in a tiny area that can be operated in a synchronized manner and information can be coherently transferred to multiple destinations. Here we show that synchronized and coordinated rotational switching of an entire nanomotor network can be realized by using the electric field of a scanning tunneling microscope tip. Strikingly, over 500 nanomotors can be simultaneously rotated on Cu(111) surface using the biases above 1 V at 80 K. This phenomenon is observed only in the hexagonal network due to the degeneracy of the ground state dipole rotational energy. (Submitted to Nature Nanotechnology). (2) Charge Transfer and Proximity Effects of a Nanoscale Molecular Superconductor: We investigate charge transfer and proximity effects of a (BETS)₂-GaCl₄ nanoscale molecular superconductor on a Ag(111) surface at the atomic limit. Although there is a charge injection from Ag(111) surface to the BETS molecules, the BETS still lose a net charge to GaCl₄ generating a partially filled outermost molecular orbital. Interestingly, tunneling spectroscopy data reveal quenching of the surface state electrons near the superconducting region. A gap state on the Ag(111) surface is observed, which then evolves into a superconducting gap on the molecules. (Submitted to Nano Letters). (3) Mechanical Flexure and Vibrational Maps of Sexiphenyl on Ag(111): We investigate the mechanical flexure and vibrational properties of para-sexiphenyl at single molecule level on a Ag(111) surface using scanning tunneling microscopy, and tunneling spectroscopy. Experiments reveal two low vibrational modes, which are quenched in the case of the self-assembled molecular layer. Lateral manipulations of the molecules show that the molecule can easily conform across the step and it recovers original configuration after the manipulation. (Submitted to Appl. Phys. Lett.).

Search for Novel Topological Phases in Superconductors Using Laser-Based Spectroscopy

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Funding: \$200,000 (2014)

PROGRAM SCOPE

The discovery of topological band insulators has stimulated a wide search for topological phases of superconductors, which are predicted to host Majorana zero modes at their boundaries. Recent advances have been made in engineering one- and two-dimensional topological superconductors through a proximity coupling of ordinary s-wave superconductors to semiconducting nanowires, ferromagnetic atomic chains or topological insulators. In contrast, the existence in nature of three-dimensional topological superconducting phases, which are predicted to host surface Majorana modes as well as more exotic surface topological orders, remains an open question. Unlike the case in lower dimensions, they cannot be engineered from a combination of existing known materials. The objective

of this project is to develop novel laser-based spectroscopic techniques that can be used to directly identify topological phases in intrinsically superconducting three-dimensional compounds.

FY 2014 HIGHLIGHTS

Our research to date has focused on the development of experimental techniques. (1) We completed the design and initial assembly of a laser-based angle-resolved photoemission spectroscopy (ARPES) setup for performing ultra low-temperature and high energy-resolution electronic structure mapping. This capability is important because of the low critical temperature scale (~ 1 K) and low superconducting gap energy scale (~ 1 meV) of three-dimensional topological superconducting candidates. We have achieved a sample temperature below 1 K using a custom designed He-3 ARPES cryostat and are in the process of testing our overall energy resolution, which is targeted for below 1 meV. Initial searches for three-dimensional topological superconductors will focus on layered metal chalcogenides. (2) Upon completion of the ARPES setup, we will be introducing two optical spectroscopic techniques into the same experimental chamber to probe complementary properties of the three-dimensional topological superconductor candidates: i) Nonlinear optical microscopy to perform spatially-resolved mapping of possible time-reversal symmetry broken domains; ii) Time-resolved optical reflectivity for probing superconducting gap symmetry. Preliminary tests of these two optical techniques have so far been successfully conducted on test samples mounted in our commercial He-4 optical cryostat down to a temperature of 4 K. Their integration with our He-3 cryostat will be performed next.

EARLY CAREER: Quantum Transport in Topological Insulator Nanoelectronic Devices

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Funding: \$152,251 (2014)

PROGRAM SCOPE

This proposal describes a research program designed to play a leading role in the field of nanoscale quantum electronic transport. The research addresses a current central theme in condensed matter physics: the conceptually new behavior of electrons in solids whose effective Hamiltonian is described by the Dirac equation and whose electronic properties are protected by fundamental symmetries of the materials band structure. In particular, the research objective of this proposal is to investigate novel quantum transport phenomena in topological insulators. Topological insulators (TIs) are materials with a bulk band gap but which have a conducting surface state. This surface state has two special properties: it exhibits a relativistic-like linear energy-momentum dispersion, analogous to graphene and, in addition, its conducting character is protected by time reversal symmetry. The latter confers the surface state its topological protection, i.e., the surface state remains gapless even in the presence of moderate disorder. The unique geometry, band structure and topological characteristics of the TIs have generated an extraordinary interest in the physics community and have led, together with graphene, to the emergence of a new paradigm of “relativistic” condensed matter physics. This research proposes to measure fundamental quantum phenomena, such as superconductivity, the quantum Hall effect and excitonic condensation in new regimes made possible by the TI’s 2D surface state geometry, topological characteristics and relativistic-like band structure. A crucial element of the proposal is the fabrication

and characterization of high quality thin TI devices, by using both exfoliation from single crystals and by growing TIs epitaxially by MBE. Electronic transport measurements as a function of temperature and magnetic field will reveal insights into a wealth of phenomena predicted by theory, including weak antilocalization, exotic types of quantum Hall effect.

FY 2014 HIGHLIGHTS

Our work this year focused on continuing the development on surface-sensitive probes which include tunneling and dual-gated transport spectroscopy. These are implemented in exfoliated devices of Bi_2Se_3 and $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_{1.7}\text{Se}_{1.3}$ (BSTS), respectively. In both cases, we use our development of an advanced fabrication technique based on exfoliated thin film transfer, which allows us to integrate TI layers into heterostructures including hexagonal Boron-Nitride (h-BN) and graphene. Projects we have pursued include: (i) dual-gated transport in h-BN–TI heterostructures, (ii) TI-graphene junctions, and (iii) STM measurements at the TI-graphene interface. The key accomplishment this year has been on project (i), and it resulted in a paper published in PRL. In this paper, we reported on electronic transport measurements of exfoliated $\text{Bi}_{1.5}\text{Sb}_{0.5}\text{Te}_{1.7}\text{Se}_{1.3}$ (BSTS) nanodevices with top and bottom gate electrodes. We showed for the first time that the chemical potential of the upper and lower surface states can be controlled independently, resulting in different resistance peaks when either surface chemical potential crosses the Dirac point. For thin devices, we found signatures of finite capacitive coupling between the surface states, consistent with fully depleted bulk states. We explained the data through a charging model which incorporates the finite density of states of the surface bands. Using angle-resolved photoemission spectroscopy (ARPES) as a control measurement of the surface state, this model allowed us to measure the chemical potential μ and charge density n of a topological surface state as well as the inter-surface capacitance. At high magnetic fields, increased field penetration through the surface states is observed, strongly suggestive of the opening of a surface state band gap.

Correlated Electrons in Graphene at the Quantum Limit

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Funding: \$525,000 (2014-2016)

PROGRAM SCOPE

Strong Coulomb interactions in low dimensions often lead to rich emergent correlated phenomena which can manifest as spontaneous breaking of the symmetry of internal quantum degrees of freedom. In graphene, the combination of real spin and pseudo (valley) spin can be described by a four-component spinor obeying $\text{SU}(4)$ symmetry. In strong quantizing magnetic fields this multi-component internal quantum degree of freedom, coupled with strong electron interactions, often results in a many-body correlated state. Examples of such correlated phases include quantum Hall ferromagnetism (QHF) and fractional quantum Hall (FQH) states, both of which present a novel hierarchy of broken symmetry states. This proposal is largely concerned with understanding the fundamental physics of electron-interaction-driven spontaneous symmetry breaking in bilayer graphene (BLG) at the quantum limit. We focus particularly on BLG, because its multi-component $\text{SU}(4)$ spin is fully experimentally controllable through electric and magnetic fields. For this purpose we investigate: (i) engineering BLG

heterostructures for high mobility and high functionality; (ii) investigating phase transitions of BLG's multi-component spin in integer and FQH states; (iii) exploring the nature of spin/valley-polarized quantum Hall edge states employing quantum point contacts and quantum Hall interferometry; (iv) studying competition between strongly correlated QHF and FQH effects in engineered and adjustable graphene superlattices; (v) realization of symmetry-protected 1-dimensional topological propagation modes in bilayer graphene; (vi) injection of cooper pairs in graphene quantum Hall edge states and investigation of the competition between proximity-induced superconducting states and Landau gap formation.

FY 2014 HIGHLIGHTS

Spontaneous symmetry breaking occurring in an interacting many body system is one of the cornerstones of modern physics. The Coulomb interaction drives spontaneous breaking of the symmetry in the internal degrees of freedom of many electron systems, leading to exotic correlated electronic states, such as the fractional quantum Hall effect (FQHE). In this period of time, we demonstrate that bilayer graphene provides a rich material platform for studying electronic interactions, hosting a variety of interacting ground states for the FQHE. Moreover, we demonstrate the capability to tune phase transitions between different ground state orderings within the FQHE states by application of a transverse electric field. To enable this, we have made innovations in graphene device preparation yielding samples of unprecedented quality, and explored correlated electronic states in these phase spaces in the quantum limit. We also report fractional QHE states in BLG that show phase transitions that can be tuned by a transverse electric field. This result provides a model platform with which to study the role of symmetry-breaking in emergent states with topological order. We believe our result to be particularly significant for 2 reasons: i) while the capability to tune phase transitions within the FQHE in graphene systems has been theoretically identified as one of the fundamentally unique interests of this material platform, this effect has not previously been experimentally accessible. ii) The capability to set the ground state order within the FQHE in bilayer graphene is predicted to have several fundamental consequences such as providing a platform to more carefully study interplay between competing phases with different topological order, and perhaps more exciting the possibility of stabilizing new exotic quantum states. The work is published in Science 345, 61-64 (2014).

Spectroscopy of Degenerate One-Dimensional Electrons in Carbon Nanotubes

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Funding: \$176,311 (2014)

PROGRAM SCOPE

We study the fundamental properties of degenerate one-dimensional (1-D) electrons in single-wall carbon nanotubes (SWCNTs) using dynamical methods to probe and understand electronic correlations and many-body phenomena. SWCNTs are an ideal 1-D system for studying novel quantum effects in nanostructures. There have been transport and optical studies on SWCNTs by a number of groups during the past decade, revealing some characteristic features of 1-D systems. However, most of the predicted exotic properties of interacting 1-D electrons have yet to be observed, and some of the

reported experimental evidence remains controversial. Here, using spectroscopic methods from the terahertz (THz) to the optical ranges, we aim to achieve a fundamental understanding of correlations and many-body effects in this prototypical 1-D nanostructure. These studies can provide a wealth of new insight into the nature of strongly correlated carriers in the ultimate 1-D limit and lead to novel nanodevice concepts and implementations.

FY 2014 HIGHLIGHTS

During FY 2014, we have made progress in three aspects of 1-D dynamic phenomena in SWCNTs: (1) Spin dynamics. We measured temperature- and power-dependent electron spin resonance in SWCNTs to determine both the spin-lattice and the spin-spin relaxation times, T_1 and T_2 . We observed that the former decreases linearly with the temperature, whereas the latter increases by over a factor of two when the temperature is increased from 3 K to 300 K. We interpreted the former as spin-lattice relaxation via interaction with conduction electrons and the latter as motional narrowing. By analyzing the latter, we found the spin hopping frequency to be 285 GHz. (2) Plasmon resonance. Plasmon resonance is expected to occur in metallic and doped semiconducting SWCNTs in the THz frequency range, but its convincing identification has so far been elusive. We performed optical, THz, and DC transport measurements on highly enriched metallic and semiconducting nanotube films. A broad and strong THz conductivity peak appeared in both types of films, whose behaviors were consistent with the plasmon resonance explanation, firmly ruling out other alternative explanations such as absorption due to curvature-induced gaps. (3) Coherent phonons. Using a macroscopic ensemble of highly enriched (6,5) SWCNTs, combined with high signal-to-noise ratio and time-dependent differential transmission spectroscopy, we generated vibrational modes in an ultrawide spectral range. A total of 14 modes were clearly resolved, we were able to identify all the observed peaks and determine the frequencies of the individual and combined modes. We provided a full summary of phonon frequencies for (6,5) nanotubes that can serve as a basic reference with which to refine our understanding of nanotube phonon spectra as well as a testbed for new theoretical models.

Dissipative and Fast-Timescale Phenomena in Superconductors

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Students: 0 Postdoctoral Fellow(s), 1 Graduate(s), 2 Undergraduate(s)
Funding: \$337,689 (2014-2016)

PROGRAM SCOPE

This project investigates rapid temporal events and transport phenomena at extreme power densities and vortex velocities, using advanced pulsed techniques developed by the PI. The PI developed a sub-nanosecond correlated time-domain current-voltage measurement, which resulted in the first real-time demonstration of ballistic supercurrent acceleration. The PI's investigations have led to the discovery/confirmation of new effects/regimes such as the hot-electron instability, flux fragmentation, quenched vortex dynamics, vortex-core explosion, current-induced depairing, etc. Besides their own novelty, these effects shed light on many key parameters and properties of the superconducting state such as gap anisotropy, electron-phonon coupling, normal-state resistivity below T_c , thermodynamic critical magnetic field, etc. Because of the uniqueness of the PI's techniques for exploring these regimes,

some of these effects have been observed only in a few materials. Finally, this research is directly relevant for practical applications since its very essence is to investigate how dissipation arises when the superconducting state is pushed to its limits.

FY 2014 HIGHLIGHTS

Two refereed publications from completed work resulted in 2014: 'Pinning mechanism in electron-doped HTS $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ epitaxial films', A. Guarino, A. Leo, G. Grimaldi, N. Martucciello, C. Dean, M. N. Kunchur, S. Pace and A. Nigro, *Supercond. Sci. Technol.* 27, 124011 (2014); and 'The mixed state of thin films in parallel fields', M. N. Kunchur, M. Liang, C. Dean and A. Gurevich, refereed book chapter in "Nanotechnology in the Security Systems (NATO Science for Peace and Security)", Chapter 2 page 15 under "Part I: Nanomaterials", Springer, ISBN-10: 9401790523, ISBN-13: 978-9401790529 (September 14, 2014). In addition, the PI gave 2 invited talks at international conferences (in Italy and Korea) and won the Donald S. Russell Award for Research in Science, Mathematics, and Engineering (the university's highest research award). Ongoing research in the past year led to the observation of two new effects in the superconductivity that occurs at the interface between the Bi_2Te_3 topological insulator and the FeTe iron chalcogenide, neither of which is itself superconducting. We have observed a transition in the current-induced depairing response as the temperature is swept through the Berezinsky-Kosterlitz-Thouless (BKT) transition, to our knowledge the first observation of its kind in such a system. The second novel result is the observation of an anomalous current-voltage response that shows a double plateau. The lower plateau exists only in the limit of very low magnetic fields and temperatures. While we are working on the detailed theory of these new effects, we were able to show that the lower plateau is associated with the Likharev explosion effect. This is the first time to see this effect in an interface superconductor, and the second time in history to confirm it at all.

Spontaneous and Field-Induced Symmetry Breaking in Low Dimensional Nanostructures

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Students: 0 Postdoctoral Fellow(s), 7 Graduate(s), 0 Undergraduate(s)
Funding: \$208,210 (2014)

PROGRAM SCOPE

Electron-electron interactions can strongly modify the qualitative properties of low-dimensional materials. This program aims at investigating and understanding strongly correlated electron behavior using carbon nanotubes and graphene, which has emerged as archetypal 1D and 2D nanostructures, via low temperature transport experiments and nanoelectromechanical measurements. The research program consists of 3 key projects: (1). symmetry-broken phases and quantum phase transitions in ultra-clean bilayer graphene (BLG); (2). symmetry-breaking, phase diagrams and stacking-order dependent transport of trilayer graphene (TLG); and (3). momentum-conserved tunneling between 2D graphene and 1D carbon nanotubes. These projects are motivated by the instability of few-layer graphene to the formation of a correlated electron ground state. A variety of states with different properties have been theoretically proposed, though the exact nature of the ground state is under intense experimental and theoretical debate. We plan to investigate and establish the nature of the ground state in BLG and TLG, using dual-gated suspended devices with mobility as high as 300,000

cm^2/Vs . We will measure the devices' electrical properties as functions of electric field, perpendicular and parallel magnetic fields, charge density and temperature, and explore possible quantum transitions among the phases. A related direction is to search for fractional quantum Hall effect and Wigner crystal states in these atomic membranes. We also plan to measure the layer polarization directly in BLG and TLG using the graphene layers as nanomechanical elements, via a technique akin to Kelvin probe microscopy, thus realizing a which-layer probe. Taken together, these proposed experiments will provide an in-depth investigation of how electron-electron interactions affect the properties of these exciting materials.

FY 2014 HIGHLIGHTS

(1) Landau level Gaps in Bilayer Graphene Landau level gaps are important parameters for quantum Hall effect in 2D materials. Using bias spectroscopy, we show that at filling factor $\nu=-2$, the gap $\Delta \sim 1.1 \text{ meV/T}$ for singly-gated geometry, and 0.17 meV/T for dual-gated geometry at zero out-of-plane electric field E_{\perp} , thus suggesting that the $\nu=-2$ state strongly depends on E_{\perp} . Our studies, published by Nano Letters, provide the first measurements of the gaps of the broken symmetry QH states in BLG with controlled layer polarization. (2) Competing $\nu=2$ States in Bilayer Graphene Quantum Hall (QH) effect, which normally appears in strong magnetic fields B , may also appear spontaneously at $B=0$ in devices with strong interactions. An example is charge-neutral bilayer graphene that is unstable to a variety of gapped spontaneous QH states, which can be explored via their adiabatic connection to QH states with the same Hall conductivity. We find two distinct phases at filling factor $\nu=2$, stabilized by large magnetic and electric fields, respectively. The majority spins of both phases form a quantum anomalous Hall state; the minority spins form a Kekulé state with spontaneous valley coherence for phase I, and a quantum valley Hall state for phase II. Our results, published by Nature Communications, shed light on the rich set of competing ordered states in BLG. (3) Graphene Nanoelectromechanical Stochastic-Frequency Oscillators To date the physical origin of the quality factor Q in nanoelectromechanical systems remains unresolved. We explore this issue by using graphene drumhead resonators, whose Q is found to scale inversely with temperature. This is understood by a model of thermally fluctuating high frequency modes that broaden the spectral response of the fundamental mode through nonlinear coupling. Our results provide a general framework for understanding dissipation and spectral line broadening in atomically thin membrane resonators. This work is published by Nano Letters.

EARLY CAREER: Transport Studies of Quantum Magnetism: Physics and Methods

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Funding: \$153,310 (2014)

PROGRAM SCOPE

Controlling the electrical properties of materials by manipulating their spin structure is a key feature in the field of magnetism research and applications. The unusual spin textures found in inversion symmetry broken magnets, e.g. Skyrmions and the Chiral Soliton lattice are of particular interest due to their stability granted by their topology. Our work focuses on the magnetotransport properties of two systems with such non-trivial spin textures in inversion symmetry broken crystalline structure. In the

isotropic cubic helimagnets MnSi and Fe-doped MnSi, a pronounced topological Hall effect emerges, and is a direct result of the gauge field generated by the Skyrmin lattice. On the other hand, in the highly anisotropic helimagnet $\text{Cr}_1/3\text{NbS}_2$, a Heisenberg spin model with Dyzaloshinkii-Moriya interactions and magnetocrystalline anisotropy successfully captures the complex spin structure and shows excellent agreement with magnetization measurements. An unusual dependence of magnetoresistance on spin orientation (i.e. parallel or perpendicular to the helix direction) is attributed to a change of the electronic structure caused by spin-orbit coupling, rather than to a purely spin-related mechanism.

FY 2014 HIGHLIGHTS

First, we perform the topological Hall effect (THE) study in Fe-doped MnSi and compare it with results from pure MnSi under pressure. We find that Fe doping increases the size of THE, indicating an enhancement of the magnitude of the emergent gauge field generated by the Skyrmin lattice (SKL). This is consistent with the concurrent reduction in the length scale of the SKL. For both pressurized and doped samples, we calculate the emergent magnetic field based on the size of the measured THE and compare it with a theoretical upper bound. The ratio of these two is found constant with pressure or Fe doping, despite their quite distinct trends in suppressing magnetic ordering. This result appeared on PRB.88.214406. In a highly anisotropic helimagnet $\text{Cr}_1/3\text{NbS}_2$ (CNS), we found understanding the role of spin-orbit coupling (SOC) is crucial to controlling magnetic anisotropy, rather than the spin texture itself. We find a larger enhancement of in-plane electrical conductivity when spins are polarized perpendicular to plane rather than parallel in CNS. This is consistent with the density of states variation near the Fermi energy, from our first principles calculations. The result shows spin-orientation dependent electronic structure modification mediated by SOC leads to the changes in in-plane conductivity. We observe unusual H dependence of the Hall signal in the same temperature range. This is likely to further indicate strong dependence of electronic structure on spin orientation relative to the plane. The result is currently under review at PRX. In order to have a better understanding of the spin structure of CNS, we study a Heisenberg spin model with Dyzaloshinkii-Moriya interactions and magnetocrystalline anisotropy, which allows the ground state spin structure to be calculated for magnetic fields of arbitrary strength and direction. The magnetization measurements show excellent agreement with the predicted spin structure. This result is published in APL.105.072405.

Experimental Study of Superconductivity in Reduced Dimensions and in Novel Materials

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Funding: \$135,000 (2014)

PROGRAM SCOPE

The overall goal is to expand our experimental understanding of quantum fluctuations in the vicinity of continuous quantum phase transitions through an exploration of ultrathin, effectively two-dimensional films of cuprate superconductors and other superconductors. Theoretically, the understanding of quantum fluctuations is under development. In superconductors quantum fluctuations take the form of zero-point motion of quantum vortex-antivortex pairs, and perhaps other objects, especially in cuprates where the underlying physics of normal state is complicated (enriched?) by the pseudogap in the

electron excitation spectrum. Experimentally, we grow ultrathin films of YBCO and BSCCO by pulsed-laser-deposition (PLD) and pursue a suite of electron transport measurements including superfluid density, resistivity, and most recently, critical cooper pair momentum. Quantum fluctuation effects are expected in the magnitude and temperature dependence of the superfluid density and the critical cooper pair momentum.

FY 2014 HIGHLIGHTS

(1) We benchmarked our novel technique for determining the superconducting coherence length, ξ , in superconducting films from measurement of the critical cooper-pair momentum. The technique involves inducing a supercurrent density comparable to the theoretical maximum, where vortices necessarily appear, by applying a large current to a small superconducting coil adjacent the film. That is, we operate our two-coil apparatus way beyond the linear-response regime. Benchmarking was done on thin Nb and amorphous MoGe films, both being conventional superconductors. It was published in Physical Review B. We had published the theoretical underpinning for the technique in PRB the previous year. (2) We measured the critical cooper-pair momentum, p_c , in a number of strongly-underdoped, very thin films of the cuprate superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. We found that p_c is linearly proportional to the superconducting transition temperature, T_c , thereby establishing that the important energy scale for superconducting cooper pairs is $k_B T_c$. In retrospect this seems obvious to some, but spectroscopy identifies two other important energy scales, so this result is significant. A paper on this work is available on ArXiv, but is not yet published. (3) In very thin cuprate superconducting films, we consistently observe a significant temperature range between where resistivity seems to go to zero and the lower temperature where superfluid density appears. The effect is absent from thicker films. The physics of this state is at present unknown.

EARLY CAREER: Probing High Temperature Superconductors with Magnetometry in Ultrahigh Magnetic Fields

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PROGRAM SCOPE

The goal of the program is to investigate the high-field magnetic properties of high temperature superconductors, materials that conduct electricity without loss. High temperature superconductivity discovered in Fe-based and Cu-based materials has been a treasure trove for condensed matter physicists. The relatively high transition temperature T_c , critical field, and critical currents indicate many possible applications in energy transfer and conservation. More importantly, the investigation of the origin of the superconductivity leads to various breakthroughs in fundamental physics. Moreover, in both cuprates and Fe-based materials, superconductivity arises by doping an antiferromagnetic state. Precise measurement of the magnetization M in ultrahigh magnetic fields will shed light on the magnetic ground state, the superconducting property, and the interaction between them. To achieve the goal, torque magnetometry will be adapted to ultrahigh magnetic field up to 100 T in the pulsed magnetic field facilities in Los Alamos National Laboratory (LANL). Major challenges for research in the pulsed field

facilities are 1) the vibrational and electrical noise, 2) difficulty stabilizing temperatures in elevated temperature ranges, and 3) short magnetic field pulses as narrow as milli-seconds. These conditions exclude some common approaches based on resonating oscillators or piezo resistors. We propose several technical innovations to advance the high frequency capacitance bridge technique to precisely measure the magnetic torque in pulsed magnetic fields. The major innovations include, 1) home-built capacitance bridge working the best from 10 kHz to 10 MHz measurement frequencies, and 2) cold amplifier near the sample to eliminate the large shunt capacitance and to greatly enhance the bridge balancing signal.

FY 2014 HIGHLIGHTS

Samarium hexaboride SmB_6 is a paradigm of strongly correlated mixed valence leading to an insulating ground state. Using torque magnetometry my group observed quantum oscillations from the conductive surface states. Results reveal that the quantum oscillation frequency is proportional to the inverse of the sinusoidal function of the magnetic field tilt angle. This confirms that the electronic state is two-dimensional, as expected for a surface state. High field measurements further reveal that the Landau Level index in the infinite field limit is $-1/2$, a Berry phase contribution in Dirac systems just like that of graphene. One big achievement is the development of a tool that directly measured the magnetization of the surface states. Traditional experimental tools to study surface states are photoemission, tunneling, and electrical transport properties. Using our advanced magnetometry technique, we determined the surface state magnetization. The results provide a novel experimental method to detect the surface electronic state of quantum materials.

Studies of Multiband and Topological Superconductors

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PROGRAM SCOPE

This project has two goals. One is to investigate the effect of scattering on the superconducting energy gap features and the proposed interband mode of multiband superconductors through electron tunneling. The other is to investigate the topological superconducting state in proximity induced superconductivity in topological insulators. For the multiband superconductivity, we have mainly focused on MgB_2 , which is the first well established multiband superconductor with clearly distinguishable two gaps. For the topological superconducting state, we have mainly focused on Bi_2Se_3 and Bi_2Te_3 nanowire and nanotubes in contact with conventional superconductor leads. Owing to the discovery of superconductivity in MgB_2 and iron pnictides, multiband superconductivity has gained tremendous attention recently. Many new physical phenomena, such as the “Leggett mode”, interband interference, soliton, and Andreev bound state, have been proposed. They are collective modes due to phase relationship or fluctuations between bands. It is also known that the scattering will smear out the energy gaps and other physical signatures in a multiband system. Due to the advance in MgB_2 thin film deposition using hybrid physical chemical vapor deposition (HPCVD) developed at Penn State, very clean thin films have been achieved with a long electron mean free path and very low scattering rate. In this

project, we have showed that MgB_2 does not just have two gaps as previously thought. Each band has a distribution of gap values associated with different parts of the Fermi surface, depending on the momentum directions. We will study how the scattering affects the distribution of energy gaps. We will use focused ion beam and electron beam lithography to create nanometer sized superconducting contacts on the topological insulator nanowire and nanotubes to study the characteristic features of the induced superconducting state.

FY 2014 HIGHLIGHTS

(1) Proximity-effect induced superconductivity in $\text{NbSe}_2/\text{Bi}_2\text{Se}_3$ heterostructures has been studied using a point contact Andreev reflection (PCAR) spectroscopy technique at low temperatures down to 40 mK. In samples with high contact interface transmission, Andreev reflection is observed with the differential conductance (dI/dV) increases at the NbSe_2 energy gap when the temperature is below its $T_c \sim 7.2$ K and a proximity induced gap in Bi_2Se_3 below ~ 5 K. In samples with intermediate contact transmission, the spectra is close to tunneling and the superconducting gaps near the surface of Bi_2Se_3 within the proximity coherence length are obtained as a function of Bi_2Se_3 thickness. In addition, at very low temperatures below 100 mK, the spectrum cannot be fitted with the standard BTK model and we speculate that this may be due to the induced topological superconducting surface states. (2) We have successfully synthesized topological insulator Bi_2Te_3 nanotubes by a solution phase method through the mechanism of Kerkendall Effect. Nanotube geometry can optimize the surface to bulk volume ratio of topological insulators and minimize the bulk conduction in the transport properties. Single crystal Tellurium nanowires were first obtained by reducing TeO_2 and then bismuth compound, as a precursor, was added into the solution. The nanotubes with inner hollow structure are formed due to the large difference of the diffusion constant between the elements. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) studies confirm the nanotube structure with typical outer diameter ranging from 90 nm to 200 nm and wall thickness around 10 to 15 nm. The typical length is about 5 – 15 μm . The temperature dependence of conductance of a single nanotube shows very insulating behavior. This is very different from the typical Bi_2Se_3 thin films and nanowires, which are often metallic due to Se vacancies.

Engineering of Mixed Pairing and Non-Abelian Majorana States of Matter in Chiral p-wave Superconductor Sr_2RuO_4 and Other Materials

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Funding: \$130,000 (2014)

PROGRAM SCOPE

This project deals with unconventional superconductivity, the consequences of and the mechanism for such unconventional superconductivity, and other novel phenomena in Sr_2RuO_4 and related ruthenates, and monolayer FeSe grown on SrTiO_3 . While few people doubt the spin-triplet nature of superconductivity in Sr_2RuO_4 , the precise pairing symmetry, namely, how the superconducting order parameter is varied on the entire Fermi surface, is yet to be determined. The first goal of this project is to establish the precise pairing symmetry in pure Sr_2RuO_4 and that in the related system of the Ru-

Sr_2RuO_4 eutectic phase (the 3-K phase); Our second goal is to explore the consequences of exotic pairing symmetries in these two material systems and establish the presence of some novel topological objects, including gapless chiral surface states, domains and domain walls, half-flux-quantum vortices that support the Majorana mode; Our third goal is to gain insight into the mechanism of superconductivity in Sr_2RuO_4 and $\text{Ru-Sr}_2\text{RuO}_4$ - How are unconventional pairings including mixed pairing states are realized in a real material? To accomplish these goals, we propose to: 1) perform phase-sensitive measurements on k_z -dependence of the order parameter for Sr_2RuO_4 ; 2) detect the presence of chiral edge states in Sr_2RuO_4 ; 3) search for a mixed pairing state in the $\text{Ru-Sr}_2\text{RuO}_4$ eutectic phase; and finally, 4) perform Little-Parks resistance oscillations and scanning SQUID measurements to search for half-flux-quantum flux states in mesoscopic samples of Sr_2RuO_4 . In addition, we will also investigate compounds closely related to Sr_2RuO_4 , such as $\text{Sr}_3\text{Ru}_2\text{O}_7$, and single crystalline films of FeSe grown on $\text{SrTiO}_3(001)$ that features a very high transition temperature.

FY 2014 HIGHLIGHTS

In 2014 we focused on the search of half-flux-quantum Little-Parks (L-P) oscillation in mesoscopic rings of Sr_2RuO_4 and the study of band-dependent electronic and magnetic properties of single crystals of $\text{Sr}_3\text{Ru}_2\text{O}_7$. Recent cantilever magnetometry measurements on micron-sized, doubly connected crystals of Sr_2RuO_4 have indicated that a half-flux-quantum state may be present in this material. To provide independent evidence for the presence of this new topological object by electrical transport measurements and examine its stability we carried out the L-T measurements which should trace out the phase boundary of the mesoscopic rings of Sr_2RuO_4 fabricated using a combination of mechanical exfoliation of Sr_2RuO_4 crystals, photolithography, and focused ion beam techniques. Without an in-plane magnetic field, large-amplitude resistance oscillations of a full-flux quantum were found as ramping the out-of-plane field. When the in-plane field and the measurement current were sufficiently large, a pronounced second set of resistance peaks consistent with the existence of half-flux-quantum states was observed in one sample. Measurements on additional samples suggest that the half-flux-quantum states, if indeed present, are likely to be metastable. In addition, we have studied the bilayer member of the Roddlesden-Popper(R-P) series, $\text{Sr}_3\text{Ru}_2\text{O}_7$, closely related to the single-layer member, Sr_2RuO_4 but non-superconducting. A band-dependent metamagnetic transition and heavily renormalized quasiparticle properties may be relevant to superconductivity in Sr_2RuO_4 . We carried out angle-dependent magnetoresistance and magneto thermoelectric measurements on crystals of $\text{Sr}_3\text{Ru}_2\text{O}_7$ cut along two specific crystalline directions and a magnetic field rotating in the ab plane. We found evidence supporting the presence of spin-momentum locking and the emergence of a coherent state with unconventional magnetism phase formed in a two-dimensional band in $\text{Sr}_3\text{Ru}_2\text{O}_7$.

Time-Resolved Spectroscopy of Insulator-Metal Transitions: Exploring Low-Energy Dynamics in Strongly Correlated Systems

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Funding: \$60,000 (2014)

PROGRAM SCOPE

Our research program focuses on the study of the large interfacial magneto-electric coupling effect and coherent spin dynamics in complex multiferroic oxide heterostructures using interface-specific and time-resolved nonlinear-optical techniques. The goal of these studies is to elucidate the static and dynamic magnetic interactions and their correlations with the electronic structure and strain states at the valence and lattice mismatched interfaces, which can be artificially engineered. Building on key advances of the previous award period, our program concentrates on two major themes: (i) to determine the interfacial magneto-electric coupling mechanism and its correlation with charge transfer, orbital states and strain states induced by the substrate or film thickness using the interface-specific magnetization-induced second-harmonic generation (MSHG) technique, and (ii) to investigate its effect on the coherent spin precession in these strongly correlated systems as a new path for fast magnetic switching utilizing the time-resolved magneto-optical Kerr effect (MOKE) technique. The science addresses issues of energy dissipation and the coupling between electronic and magnetic order in such advanced materials, of fundamental importance to our understanding of solid-state properties and has numerous applications.

FY 2014 HIGHLIGHTS

The sensitivity of the electronic and spin state of strongly correlated oxides to charge provides enhanced coupling between magnetic and ferroelectric order parameters; it often relies on charge doping of a colossal magneto-resistance manganite to modulate between high and low spin state, which compete for the ground state of the system. However, the microscopic origin of this effect is still not fully understood. The optical MSHG technique is particularly effective for probing the magnetic state at buried interfaces, and thus turns out to be suitable for investigating the interfacial magneto-electric coupling mechanism. We have investigated the interfacial spin state of the multiferroic heterostructure $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3 / \text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ (PZT/LSMO) and its dependence on ferroelectric polarization with MSHG at 78 K. The magnetization in the first unit cell layer at the interface can be widely tuned over an order of magnitude by varying the applied electric field by 180 kV/cm. The cross-coupling between ferroelectric and ferromagnetic behavior at the heterointerface is mainly electronic, due to charge injection. The ferroelectric polarization of PZT can tune the spin alignment of Mn ions at the heterointerface from ferromagnetic to antiferromagnetic exchange coupled. In contrast, the bulk magnetization probed with MOKE remains unchanged. Multiple domains of ferromagnetic to antiferromagnetic phase coexist as the ferroelectric polarization of PZT is switched. We believe our results provide new insights into the interfacial spin-charge coupling.

Establishing the Consequences of Intertwined Order Parameters in Spatially Modulated Superconductors

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Funding: \$431,666 (2014)

PROGRAM SCOPE

Over a surprisingly diverse set of materials, unconventional superconductivity (SC) resides near the boundary of some other ordered phase exhibiting broken translational symmetry, such as antiferromagnetism, charge or orbital order. It is commonly thought that these order parameters compete with SC, however there is widespread evidence that some optimal degree of inhomogeneity may, in fact, be favorable for SC in some cases. Moreover, recent transport and magnetization experiments on the classic, stripe-ordered superconductor $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ indicate that the interaction between charge order and SC is coherent, implying that the interaction between SC and alternate orders is more nuanced than previously thought. Subsequent work has shown, on pure symmetry grounds, that if the interaction between SC and charge order is coherent, several other highly novel phenomena should also exist, which can be readily explored with a combination of existing experimental techniques. The purpose of this project is to establish the generality and full implications of the presence of coherent, phase-dependent coupling between charge and SC order in unconventional superconductors. This will be accomplished with a set of experiments designed to detect several predicted phenomena, including neutron scattering and growth of single crystals, scanning SQUID microscopy and Josephson interferometry, Raman scattering, and x-ray scattering. These experiments will comprise an exhaustive test for coherent interference phenomena in several distinct material systems. If successful, this project will establish for the first time the physical origin of the sometimes perplexing relationship between SC and other forms of order in unconventional superconductors. It will also lead to the discovery of several new phenomena not previously observed in any condensed matter (CM) system. If not observed, the negative results will set strong constraints on the types of interactions that take place in unconventional SC.

FY 2014 HIGHLIGHTS

Recent months have seen headway in materials development, experimental and theoretical aspects of this program. PI MacDougall has begun preparations for the production of single crystals across the doping series of stripe-ordered $\text{La}_{2-x-y}\text{Eu}_y\text{Sr}_x\text{CuO}_4$ via the float zone technique and Cu-intercalated TiSe_2 using chemical vapor transport, and has performed proof-of-principle growths of both. PI Van Harlingen has grown nanowires of stripe material, $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ (LBCO), and begun studying fluctuations in the resistance to explore the dynamics of charge stripes associated closely with the sharp drop in the SC T_c near $x=1/8$. He observes a sharp increase in the noise at a temperatures of 40-50K, near the where the onset of charge ordering has been previously reported by Abbamonte, and signatures in the spectral density suggestive of an origin in pinned dynamical stripes. PI Abbamonte has been studying the effect of Ti-doping on the CDW-state of TaS_2 . Using temperature dependent transport and x-ray measurements, his group has uncovered new information about the evolution of the CDW wavevector, and put forward an alternate explanation for the known resistivity anomaly at 8% doping, in terms of a commensurability effect with the lattice. A paper on this work, co-authored by all PIs, is currently under review at Physical Review B (PRB). PI Fradkin has worked on the theory of intertwined orders in high temperature superconductors. He has coauthored a review article on this subject, to appear in Reviews of Modern Physics, and a recent Physical Review Letter, in which his group showed that simple one-dimensional models that have pair density wave (PDW) ground states are actually topological SC and exhibit protected Majorana bound states at interfaces with uniform SC. On a different tack, Fradkin recently co-authored a paper in PRB on a theory of time-reversal breaking spin liquid states in the magnetization plateaus of anisotropic frustrated quantum Heisenberg antiferromagnets on the kagome lattice.

Magnetotransport Studies of Low-Dimensional Electron Systems Based on GaAs/AlGaAs Heterostructures and Graphene

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Funding: \$146,289 (2014)

PROGRAM SCOPE

Emergence is the process of complex behaviors arising out of a multiplicity of basic interactions. Emergent phenomena often exhibit remarkable, useful, and collective aspects - features which have helped to make emergent behavior a topic of current research. A high quality GaAs/AlGaAs two-dimensional electron system subjected to modest microwave/terahertz photo-excitation at low temperature exhibits radiation-induced zero-resistance states at small magnetic fields, and this phenomenon has been cited as evidence for emergence in a driven, steady state non-equilibrium context. Since the initial observations, photo-excited electronic systems have become a popular arena to search for new physical phenomena. The prime objectives of this research are to (a) uncover novel emergent phenomena in the photoexcited GaAs/AlGaAs electronic system and (b) elucidate the electronic properties of graphene and other 2D materials using photo-excited transport in the near-to-equilibrium context. The study of high mobility GaAs/AlGaAs heterostructures will help to provide a better understanding of the physics of zero-resistance states and associated magnetoresistance oscillations. The microwave photo-excited transport studies of graphene will serve to characterize spin properties through the resistive detection of spin resonance. Such a study will expand our empirical knowledge of steady state non-equilibrium electronic transport, provide a better understanding of basic interactions that leads to the emergence of the microwave-induced zero-resistance states in the two-dimensional electron system, and provide new insight into the response of the novel 2D materials to microwave and terahertz radiation while illuminating upon, for example, the spin characteristics of massless Dirac fermions.

FY 2014 HIGHLIGHTS

Some highlights: (a) Transport characteristics of a negative magneto-conductivity state - Negative diagonal magneto-conductivity/resistivity is a spectacular property of driven, far-from-equilibrium, low dimensional electronic systems. Yet, the physical response of this exotic electronic state is not yet fully understood since it is rarely encountered in experiment. Here, we examined numerically the magneto-transport characteristics of a negative conductivity/ resistivity state. Obtained results suggest, surprisingly, that a bare negative diagonal conductivity/resistivity state in the 2DES in a magnetic field under photo-excitation should yield a positive diagonal resistance, with a concomitant sign reversal in the Hall voltage.[R. Mani and A. Kriisa, Scientific Reports, 3, 3478 (2013)] (b) Size dependent giant magnetoresistance in mm-scale GaAs/AlGaAs devices – Observations of large changes in the electrical resistance induced by the application of a small magnetic field provide new understanding into the physical phenomena involved in the associated electronic transport. This study examined a “bell-shape” negative giant magnetoresistance (GMR) that grows in enormously in magnitude with decreasing temperatures in mm-wide high mobility 2D GaAs/AlGaAs devices. Experiments showed, remarkably,

that the span of this magnetoresistance on the magnetic-field-axis increases with decreasing device width, W , without producing a concurrent Hall resistance correction. These results were successfully reproduced in a multi-conduction model. The results suggested that a size effect in the mm-wide 2DES with mm-scale electron mean-free-paths is responsible for the observed effects. [R. Mani *et al.*, Scientific Reports 3, 2747 (2013)]

Superconductivity and Magnetism in d- and f-Electron Materials

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Funding: \$300,000 (2014)

PROGRAM SCOPE

This research program focuses on superconductivity, magnetism, and their mutual interaction in d- and f-electron materials. An overarching goal of superconductivity research is the discovery of materials which are superconducting at high temperature (ideally, near or above room temperature). While a theoretical approach is useful for understanding the properties of superconductors, it has not yet proven to be successful in predicting practical superconducting materials and, to date, virtually all known superconductors have been discovered through systematic experimental research. The emphasis of our research program is on the physics of superconducting, magnetic, heavy fermion, non-Fermi liquid and other types of strongly correlated electron phenomena in novel transition metal, rare-earth, and actinide based oxides and intermetallic compounds with a particular focus on the growth of high quality single crystals. The research will involve the search for new superconducting materials and the preparation of high quality single crystal, thin film, and polycrystalline specimens of high- T_c and novel f-electron superconductors. The anisotropic normal and superconducting state properties of these materials will be studied as a function of chemical composition, temperature, pressure, and magnetic field in order to obtain information about the underlying electronic, lattice, and magnetic excitations involved in the superconductivity, the symmetry of the superconducting order parameter, and the electron pairing mechanism. Phenomena associated with the interplay between superconductivity and magnetic order and vortex flux-line dynamics and pinning in the mixed state will be investigated. Neutron scattering, photoemission, infrared spectroscopy and other specialized measurements will be carried out with collaborators. This research program will contribute to furthering the understanding of the optimal conditions for the occurrence of superconductivity.

FY 2014 HIGHLIGHTS

(1) Electrical resistivity measurements under pressure to ~ 2.8 GPa on the compounds $\text{LnO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ (Ln = La, Ce, Pr, Nd) revealed a transition from a low-pressure superconducting phase to a high-pressure superconducting phase with a higher T_c (highest $T_c = 10$ K for La) at a critical pressure P_c that increased with Ln atomic number. (2) Electrical resistivity measurements on single crystals of LaFeAsO under pressure revealed a decrease of the spin density wave (SDW) transition temperature with pressure towards 0 K at $P \approx 10$ GPa, but no evidence for superconductivity above 1 K up to $P \approx 37$ GPa. (3) Penetration depth measurements on single crystals of $\text{Ce}_{1-x}\text{Yb}_x\text{CoIn}_5$ revealed a crossover from nodal to nodeless superconductivity near $x \approx 0.2$, the concentration where an Yb valence transition, suppression

of the quantum critical field, and a Fermi surface reconstruction occur (the actual composition is 1/3 of the nominal concentration x up to $x \sim 0.5$). (4) NMR measurements on URu_2Si_2 yielded evidence for the formation of a pseudogap between the hidden order (HO) transition temperature of 17.5 K and 30 K. Experiments on $URu_{2-x}Os_xSi_2$ suggest a phase transition at $x \approx 0.2$ from the HO to the antiferromagnetic phase. (5) Kondo disorder in the filled-skutterudite system $CePt_4Ge_{12-x}Sb_x$ that governs the physical properties and emergence of non-Fermi liquid behavior and antiferromagnetic order was studied by means of thermoelectric power measurements. (6) Eleven new Cd-based compounds with chemical formulas RNi_2Cd_{20} ($R = Y, La, Nd, Sm, Gd, Tb$) and RPd_2Cd_{20} ($R = Ce, Pr, and Sm$) were synthesized in single crystalline form. (7) Electrical resistivity measurements under pressure revealed that pressures of 55 GPa were insufficient to close the energy gap of Sr_2IrO_4 , while pressures up to 60 GPa reduced the electrical resistivity of $Sr_3Ir_2O_7$ at 10 K by five orders of magnitude. Further increases in pressure up to 100 GPa were unable to completely close the Mott energy gap and induce a metallic state in $Sr_3Ir_2O_7$.

Controlling Superconductivity via Tunable Nanostructure Arrays

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Funding: \$733,333 (2014-2015)

PROGRAM SCOPE

The goal of this proposal is to understand and control how collective behavior emerges in exotic superconducting systems. To achieve this, we precisely control the configuration and coupling of islands of superconductors patterned on conducting substrates, to develop tunable, proximity-coupled nanostructure arrays that emulate quantum phases observed or predicted in bulk materials. Array parameters that are tuned include disorder, lattice configuration, geometric frustration, and dimension. These studies aim to clarify the factors that diminish or enhance superconductors' critical properties. Further, the studies focus on controlling these parameters to induce novel phase regimes, such as pseudogap-like phases, 2D metallic states and Fulde-Ferrell-Larkin-Ovchinnikov (FFLO) phases. The research combines temperature- and field-dependent transport measurements with magnetic resonance force microscopy measurements of local vortex spatial structure and surface currents. This combination of probes, along with accurate phenomenological modeling, can provide complete characterization of the phase behavior (e.g., superconducting, strange metal, strange insulator, etc.) of the samples, and allows the determination of how different island interactions lead to different collective phenomena.

FY 2014 HIGHLIGHTS

We have made progress on multiple fronts, including understanding the superconducting behavior of single mesoscopic islands, determining the vortex dynamics of island arrays, and developing a new method of imaging surface currents. In studying single, mesoscopic, granular superconducting islands, we found that the onset of superconductivity is determined by the size of the largest grain within each island, rather than by charging effects or just bulk transition temperature. The results explain how superconductivity can be suppressed in surprisingly large systems, and clarify the behavior of disordered

or granular superconductors. We also studied the behavior of vortices in island array systems having an applied perpendicular magnetic field. By combining experiment with phenomenological modeling we could understand an unusually wide range of vortex-dominated transport behavior. Additionally, we noticed a particular vortex transport regime that was not accurately described by our model, which may have an unconventional origin, and which will be further examined via transport and imaging. Finally, we have developed a high sensitivity magnetic force microscopy (MFM) method to image surface currents with a sensitivity in the nano-Tesla range and sub-micron spatial resolution. We have demonstrated this technique by imaging the current flow in micron-scale patterned metal wires. Our immediate goal is to use this technique to study the spatial distribution of surface currents in the superconducting island arrays in the mixed superconducting-normal state.

Spectroscopic Investigation of Novel Electronic and Magnetic Materials

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Funding: \$147,845 (2014)

PROGRAM SCOPE

The goal of our research program is to develop a fundamental understanding of the mechanisms underlying the interplay between charge, structure, and magnetism in complex materials. This insight facilitates the development of tunable multifunctional solids and nanomaterials, which are scientifically and technologically important. Our main strategy involves investigating the dynamic response of functional materials like multiferroics, quantum magnets, frustrated systems, and compounds containing domain walls or 4- and 5d centers, and we perform these measurements under external stimuli (like high magnetic fields and pressures) and at very small sizes where quantum confinement becomes apparent. By so doing, we learn about the relationships between different ordered and emergent states, explore the dynamic aspects of coupling, and gain insight into the generality of these phenomena and their underlying mechanisms. In addition to broadening the understanding of novel solids under extreme conditions, multifunctional materials and their assemblies are of interest for light harvesting, spintronic, and solid state lubrication applications.

FY 2014 HIGHLIGHTS

Several exciting discoveries were made under the auspices of our Department of Energy-supported program during the past year. Briefly, they include (i) revealing the magnetic field-induced shift of the optical band gap in $\text{Ni}_3\text{V}_2\text{O}_8$, (ii) testing the role of combined frustration and spin-orbit interactions on field-induced color change mechanisms in $\text{R}(\text{In},\text{Mn})\text{O}_3$, (iii) uncovering the dynamic signatures of domain walls in multiferroic ErMnO_3 , (iv) analyzing the electronic structure of a series of spinel ferrites, (v) unraveling size-dependent vibronic coupling in nanoscale $\alpha\text{-Fe}_2\text{O}_3$, and (vi) investigating the Burstein-Moss effect in Re-substituted MoS_2 nanoparticles. What brings these findings together is the interplay between charge, structure, and magnetism and the spectroscopic techniques with which we investigate these phenomena. A broad range of educational, outreach, and service activities also took place under the auspices of this Department of Energy grant. The majority were in the area of conference organization (2013 Telluride workshop on spin-orbit coupling in 4- and 5d materials and the 2014

Gordon Research Conference on multiferroic and magnetoelectric materials) and service to the National High Magnetic Field Laboratory and the National Synchrotron Light Source.

Nanostructure Studies of Strongly Correlated Materials

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Funding: \$140,000 (2014)

PROGRAM SCOPE

Over the last two decades nanofabrication techniques have advanced significantly, and nanostructure-based methods have enabled great advances in our fundamental understanding of the physics of electrons in conventional metals and semiconductors such as Si and GaAs. In this program, we apply these nanostructure-based approaches to strongly correlated electronic materials, systems in which the electron-electron interactions can dominate the electronic, magnetic, and thermodynamic properties of the material. Specific materials of interest are those that exhibit metal-insulator transitions, when the conductivity of the material changes dramatically as the temperature is shifted through a transition that may include a structural component. Specific materials under examination include: vanadium dioxide (VO_2), layered dichalcogenides (TiSe_2), and rare earth nickelates (e.g., NdNiO_3). All three of these materials have high temperature conducting states and low temperature insulating states. We are using nanostructure techniques (very closely spaced electrodes to observe the electric-field-driven stability of the insulating phase; studies of contact resistance to gain insight into the injection and removal of charge from correlated materials above and below the transition; ionic liquids and hydrogen intercalation to tune charge density and hence the state of the material) to gain insights into the underlying physics behind the transitions and the relevant ordered states. We are also using nanostructure methods to examine emergent magnetism in related correlated materials (e.g., Fe-intercalated TaS_2), and mesoscopic electronic transport in materials where the Fermi liquid theory, the conventional model of metals, seems to fail (e.g., the hydrogen-doped “bad” metal H_xVO_2).

FY 2014 HIGHLIGHTS

In the past year (ending 9/30/14) we have had several successes in this program. Through collaborative investigations with a synchrotron/neutron scattering group, we have determined the phase diagram and precise structures of hydrogen-intercalated H_xVO_2 . We find that hydrogen intercalations as large as $x=0.6$ are possible, and that the stabilization of a “bad” metal phase (and the complete elimination of the metal-insulator transition of VO_2) takes place through doping of the vanadium 3d band (Mott physics) rather than changes in lattice stability (Peierls physics). This work has been published in the Journal of the American Chemical Society. We also investigated the kinetics of hydrogen diffusion in single-crystal VO_2 nanowires. We found that H diffusion along the (rutile) c-axis is far faster than transverse to that axis; moreover, we found that H diffusion is significantly more rapid in the rutile (metallic) structure than in the monoclinic (insulating) structure, even when accounting for temperature effects. This work has been published in Nano Letters. We have examined electronic transport from the micron to the nanoscale in NdNiO_3 films. At low temperatures we find a crossover from conventional Ohmic response to nonlinear conduction that appears consistent with the correlated equivalent of

Landau-Zener breakdown. This work has been published in Phys. Rev. B. We have also examined the remarkable magnetism and associated magnetoresistance in Fe_xTaS_2 , through a collaboration with Prof. Emilia Morosan. We have found a magnetization-switching magnetoresistance approaching 100% (!) at low temperatures, and it appears that the mechanism is spin-disorder scattering in the presence of strong spin-orbit coupling; this is a previously unreported mechanism that may provide a path toward technologically useful magnetoresistive materials. This work has been submitted for publication.

EARLY CAREER: Exploring Superconductivity at the Edge of Magnetic or Structural Instabilities

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Funding: \$750,000 (2014-2018)

PROGRAM SCOPE

This project aims at understanding the interplay among structural, magnetic and electronic degrees of freedom in unconventional superconductors, a class of materials in one of the most challenging and interesting areas of condensed matter physics. Compared with conventional superconductors, unconventional superconductors have not been explained by current theories and typically exhibit high critical temperatures (T_c 's), meaning they can conduct electricity with low losses, some of which can do this at or above liquid nitrogen temperatures. This property makes them of particular use for applications in energy generation and electrical energy transmission. These materials are also of fundamental scientific interest because the existence of structural, magnetic, orbital/charge and superconducting orders provides a platform in understanding and ultimately manipulating these interactions. Therefore the objective of this research project is to design, fabricate and characterize new superconducting materials, including the iron-based superconductors that lie at the edge of structural/magnetic instability using solid state reaction, crystal-growth methods, electrical transport and thermodynamic measurements with/without magnetic field. The goal of this research project is to help understand the relationship among different orders in these materials, to examine the structure-property relationship, and to shed light on the electron-electron interactions responsible for the superconducting phase transition.

FY 2014 HIGHLIGHTS

We have three major projects going on: (1) We have successfully grown and characterized two new series of Fe-based superconductors, the Co and Ni doped 10-3-8 superconducting family. The structural/magnetic phase transitions in the parent compound were suppressed to lower temperature and superconductivity up to 15 K occurs. The comparison between the two families shows rigid band approximation is applicable here. T_c is relatively lower in Ni doped 10-3-8, may be due to the strong impurity scattering from Ni atoms comparing to Co dopants. No coexistence between superconductivity and magnetism is observed. Considering the fact that coexistence occurs for more isotropic 122 and no coexistence for anisotropic 1111 Fe pnictide families, this may suggest the importance of interlayer coupling in the interplay of magnetism and SC. (2) We have successfully grown high quality single crystals of $\text{Ca}_{0.73}\text{La}_{0.27}\text{FeAs}_2$, the 'parent'/overunderdoped compound of the 112 superconducting family. We found there is a monoclinic to triclinic structural phase transition at 58 K and a paramagnetic to

stripe AFM phase transition at 54 K. Unlike other parent compounds of cuprates and Fe-based superconductors, without external stress/magnetic field, this material naturally remains a single structural domain with fixed crystallographic a and b directions below 58 K. In this single structural domain, S-type magnetic domain walls form with spin direction rotating 90° across the domain wall. The fact that the spin orientation is 45° from the stripe direction, instead of 90° as in other Fe pnictides, may indicate this material has weaker spin-orbital coupling. (3) New 112 superconductors with T_c up to 20 K are discovered. This is a new route to lead to SC in the 112 family. This discovery made the systematic study of nematic fluctuation without external pressure possible for Fe pnictide.

Mapping the Electron Response of Nanomaterials

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Funding: \$211,000 (2014)

PROGRAM SCOPE

This program has the goal of understanding the physics of emergent properties in artificially nanostructured low-dimensional systems. To accomplish this goal, we are focused on (1) preparing large surface arrays of 1D and 2D systems, such as monatomic wires synthesized by self-assembly and freestanding monolayer films formed via exfoliation techniques or epitaxial CVD, and (2) examining their physics using advanced photoemission techniques, i.e., small-spot, time-resolved, or high-resolution, and atomic resolution low- and variable-temperature STM probes. Finally, a major component of this effort involves a simultaneous theoretical effort using the concepts and tools of many body physics as well as DFT computations. Examples of some of the important questions our work is trying to answer include: Are there new electronic phases near surfaces in one-atom-wide wires or in nanoparticles, and can theoretical constructs be developed to examine such systems? What are the emergent dynamic properties arising from lateral confinement in 1D and 2D confined systems? Can we probe many-body effects in exfoliated freestanding graphene and in other exfoliated materials such as oxides or topological insulators?

FY 2014 HIGHLIGHTS

We have continued our investigations of monolayer and few layer transition-metal dichalcogenides. In the previous year, we had investigated the thickness dependent electronic structure of substrate supported MoS₂. This year, we directly measured the electronic structure of suspended exfoliated monolayer molybdenum disulfide (MoS₂) using micrometer-scale angle-resolved photoemission spectroscopy. Measurements of both suspended and supported monolayer MoS₂ elucidated the effects of interaction with a substrate. A suggested relaxation of the in-plane lattice constant was found for both suspended and supported monolayer MoS₂ crystals. For suspended MoS₂, a careful investigation of the measured uppermost valence band gave an effective mass at Gamma and K of 2.20m₀ and 0.42m₀, respectively, and a fitted band spin-orbit splitting at K of 129 meV. We have also investigated other transition-metal dichalcogenides. Specifically, we performed angle-resolved photoemission spectroscopic measurements of the evolution of the thickness-dependent electronic-band structure of the heavy-atom two-dimensional layered, dichalcogenide, tungsten-diselenide (WSe₂). Our data, taken

on mechanically exfoliated WSe₂ single-crystals, provided direct evidence for shifting of the valence-band maximum from Gamma (multilayer WSe₂), to K, (single-layer WSe₂). Further, our measurements also set a lower bound on the energy of the direct band-gap and provided direct measurement of the hole effective mass. We have initiated other photoemission experiments on correlated electron oxide crystals.

Exploring Photon-Coupled Fundamental Interactions in Colloidal Semiconductor Based Hybrid Nanostructures

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Funding: \$128,194 (2014)

PROGRAM SCOPE

The interplay between photon and matter is the basis of many fundamental processes and various applications. Harnessing light-matter or even more exotic light-matter-spin interactions can allow new underlying physical principles as well as technologies of solid-state quantum information processing. This program is aimed at gaining an improved understanding of emerging fundamental photon-coupled processes at the nanoscale with particular emphasis on photon and spin-related interfacial coupling of semiconductor on the ensemble level. This program involves integration of various far-field time-resolved optical spectroscopies with recent nanoscale materials advance of precisely tailored zero-dimensional colloidal semiconductors based hybrid nanostructures possessing different functionality.

FY 2014 HIGHLIGHTS

(1) We have achieved a new class of colloidal hybrid nanostructures with well-defined intra- synergistic coupling interactions that can offer tunable nanoscale colloidal condensed matter systems for understanding a few photon-coupled fundamental processes on the ensemble level, and performing ultrafast far-field all-optical measurement and spin manipulation in hybrid core-shell nanostructures based on (ac) optical Stark effect (ac-OSE). A hybrid nanostructure is defined as a nanoscale unit that can integrate various functional units (such as semiconducting, metallic and magnetic quantum dots) with internal synergistic coupling. We have particularly focused on controlling fine parameters of hybrid nanostructures including anisotropy, symmetry, composition, and structural order, which are critical for materials characteristics. The progress includes both development of a hierarchical synthetic approach for controlling the structural order of non-centrosymmetric hybrid nanooligomers (Nature Commun. 5, 4792, 2014) and morphology imprinting synthetic strategy for centrosymmetric hybrid core-shell nanostructures, with independent control of anisotropic core and shell (manuscript in preparation). (2) We have made substantial progress towards demonstration of all optical ultrafast coherent manipulation of fundamental physical processes in complex colloidal nanostructures by light-matter interactions. The progress includes all optical manipulation of both phonon and spin dynamics in colloidal nanostructures for the first time. For example, by utilization of multiple femto-second pulses the selective phonon mode can be enhanced or suppressed, which can be critical for understanding various phonon-related nanoscale physical phenomena (manuscript in preparation).

EARLY CAREER: Non-Centrosymmetric Topological Superconductivity

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Funding: \$150,000 (2014)

PROGRAM SCOPE

Superconductors without inversion symmetry, or non-centrosymmetric superconductors, promise a much more robust route to realizing topological superconducting states. With inversion symmetry being one of two key symmetries for Cooper pairing (time reversal being the other), its absence has profound implications on the formation of Cooper pairs. With a non-trivial topology of the Bogoliubov quasiparticle wavefunction resulting in protected zero-energy boundary states analogous to those of topological insulator (TI) systems, the promise of topological superconductivity (TSC) in NC superconductors is very strong. With strong band inversion, the RPtBi and RPdBi ternary half-Heusler compounds are candidate TI systems that, as non-centrosymmetric superconductors, also have the potential to harbor mixed-parity states and are therefore unique in that they are simultaneously both TI and TSC candidate systems. We are exploring the family of rare earth-bismuthide (RPtBi and RPdBi) half-Heusler compounds, synthesizing high-quality crystalline specimens and fully characterizing their normal, superconducting and magnetic states in an effort to reveal their potential for realizing the next generation of topological insulators and superconductors. Our most recent developments include synthesis and characterization of the palladium-based RPdBi series, revealing another family of superconducting compounds in the RPdBi (R=La to Lu) series. These include non-metallic transport, low carrier densities, unconventional magnetoresistance, magnetism and superconductivity.

FY 2014 HIGHLIGHTS

Electrical resistivity and magnetic susceptibility measurements of the RPdBi series have been performed down to 20 mK temperatures, revealing an interesting progression of superconducting phase transitions that evolves with rare earth species. Intriguingly, our results on the RPdBi compounds indicate that superconductivity in this series onsets at a higher transition temperature than in the Pt-based series, with maximum superconducting transition above one Kelvin found in the non-magnetic Y- and Lu-based compounds. Furthermore, superconductivity may coexist with long-range magnetic order, as determined by neutron scattering experiments on TbPdBi, DyPdBi and HoPdBi, which all undergo antiferromagnetic ordering transitions before entering a superconducting state at a lower temperature. These results have been confirmed by AC susceptibility measurements and continue to be probed by specific heat measurements, which are challenging owing to extremely low carrier densities ($\sim 10^{18} \text{ cm}^{-3}$). Rare earth magnetism has been characterized in this series, as evidenced by transport, magnetization and specific heat signatures of bulk phase transitions, as well as neutron scattering experiments in collaboration with Dr. Jeffrey Lynn at the NIST Center for Neutron Research. Specific heat measurements have revealed a progression of the bulk magnetic transition that is consistent with order parameter studies of the magnetic phase via neutron scattering. Continuing work is studying the inelastic (crystal electric field) properties of these materials. Penetration depth measurements on the RPtBi series using the tunnel-diode resonator technique in collaboration with Prof. Ruslan Prozorov at Ames National Laboratory are being used to determine the unconventional nature of the superconducting state. In

addition, preliminary point contact spectroscopy measurements at UMD exhibit unusual characteristics of the superconducting state conductance spectrum.

Artificially Structured Semiconductors to Model Novel Quantum Phenomena

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Funding: \$200,000 (2014)

PROGRAM SCOPE

We seek the design and exploration of novel electron states in controllable artificial structures that are realized in semiconductor quantum heterostructures by advanced nanofabrication. We strive to uncover new collective states of strongly interacting electrons in artificial potential energy patterns of tunable geometry. The fabricated devices belong to a class of scalable simulators of quantum states in which the main actors are many electron systems in high quality semiconductor structures. A primary goal is to reveal striking interplays between fundamental electron interactions and geometrical constraints (topology). These interactions should be venues for creation of novel quantum states that could, eventually, lead to new device concepts. To achieve milestones in this research we strive to advance the state-of-the-art of nanofabrication of patterns superimposed on semiconductors. The honeycomb topology, or 'artificial graphene' (AG), is a benchmark of the proposed research. In AG lattices an assembly of quantum dots is in a honeycomb pattern with electron entanglement occurring via inter-dot interactions. The initial studies have focus on AG lattices designed and fabricated with exquisite precision. We seek here to achieve electron systems that display the states with energies that have relativistic-like momentum dispersion that characterize Dirac fermions, and that could have novel topologically protected behaviors. Reaching this milestone leads to research goals that we describe as creation and study of 'novel quantum states in a semiconductor chip of high perfection' At Columbia Dr. Shalom Wind leads on nanofabrication with a new 100keV e-beam nanolithography, and Prof. Aron Pinczuk leads on optical experiments at high magnetic fields and low temperature reaching to below 50mK. High quality modulation doped GaAs/AlGaAs quantum wells are the starting material for the fabrication of artificial lattices.

FY 2014 HIGHLIGHTS

We fabricated very short period (as small as 40 nm) honeycomb lattice patterns in GaAs quantum wells. These structures have a potential modulation for electron states that is described as artificial graphene (AG) because the topology of the potential is similar to that of natural graphene. The fabricated AG lattices consist of an assembly of quantum dots arranged in a honeycomb pattern that are created by e-beam lithography followed by very low damage reactive-ion-etching of GaAs quantum wells. Very small quantum dot diameters below 20nm have been achieved for the first time. The small diameter quantum dots enable the creation of AG lattices with record extremely short periods that are expected to support formation of well-defined Dirac fermion states of electrons with kinetic energy that is linear in momentum (massless). Characterization by photoluminescence (PL) from conduction to valence band optical transitions enables determinations of electron density in the fabricated AG structures. Resonant

inelastic light scattering (RILS) experiments at low temperature (about 4K) probe the ‘miniband’ structure created by the AG potential. Low-lying modes observed by RILS are interpreted as transitions of electrons from populated minibands to empty minibands. The calculated miniband structure for the AG structures with shortest period, 40 and 50nm, indicates formation of well-defined Dirac fermions. Joint density-of states evaluations based on calculated mini-band structures are in excellent agreement with RILS results from the short period AG structures. Further control over parameters such as the Fermi level should permit manipulation of massless fermions. These results demonstrate that high precision patterning of semiconductor quantum wells create a platform for explorations of novel behavior in a semiconductor quantum simulator.

Engineering Topological States of Matter and Search for Majorana Fermions

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Funding: \$175,000 (2014)

PROGRAM SCOPE

Excitations with non-Abelian statistics are non-local objects and their wavefunctions contains information about the history of topological deformations of the many-particle system. Non-locality makes them resilient against local perturbations and quantum information can be encoded by exchanging (braiding) non-Abelian particles. Development of systems where non-Abelian excitations can be created and manipulated is a step toward development of a topologically-protected fault tolerant quantum computer. Within the scope of this program we are developing and studying systems which can support non-Abelian excitations. The main objective is the development of hybrid one-dimensional wires where superconductivity is induced in the semiconductor material by proximity effects from an ordinary superconductor. In the presence of strong magnetic field in a properly designed system topological superconductivity can be realized, where Majorana modes are formed at the ends of the wire.

FY 2014 HIGHLIGHTS

The major drawback of nanowire-based proposals to realize Majorana fermions is the rigidity of nanowires and inability to perform exchanges to demonstrate non-Abelian properties. Within the last year we designed an entirely new platform where non-Abelian excitations can be created and manipulated within a two-dimensional space. At the heart of the new platform is a 2D magnetic semiconductor where Lande g-factor changes sign at high magnetic fields. The system combines topological protection of edge states of the quantum Hall effect and deterministic localization of non-Abelian excitations at the phase boundary between topologically trivial and non-trivial phases of gate-formed helical 1D wires. It also supports higher order non-Abelian excitations which are required for universal qubit realization. Key feasibility experiments have been performed where we demonstrated gate control of the quantum Hall ferromagnet polarization and extracted important spin-orbit parameters of the system.

Quantum Coherence and Random Fields at Mesoscopic Scales

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PROGRAM SCOPE

Disorder and fluctuations can combine to produce novel and important electronic, magnetic, and optical effects. Inhomogeneous quantum systems are particularly appealing in this context because they have a proclivity for self-organization on the mesoscale and can exhibit pronounced fluctuations away from equilibrium. With the right choice of materials, there are manifest opportunities for tailoring the macroscopic response and for garnering insights into fundamental quantum properties such as coherence and entanglement. We seek here to explore and exploit model, disordered and geometrically frustrated magnets where spin clusters stably detach themselves from their surroundings, leading to extreme sensitivity to finite frequency excitations and the ability to encode information. Moreover, by tuning the spin concentration and/or the quantum tunneling probability, it should be possible to study the competition between quantum entanglement and random field effects. As one passes from the quantum to the classical limit, clear implications develop for magnetic storage architectures. Finally, extensions from quantum ferromagnets to quantum antiferromagnets promise new physics as well as tests of universality and general applicability. A combination of ac susceptometry, dc magnetometry, noise measurements, hole burning, non-linear Fano experiments, and neutron diffraction as functions of temperature, magnetic field, frequency, excitation amplitude, dipole concentration, and disorder should address issues of stability, overlap, coherence, and control. We are especially interested in probing the evolution of the local order in the progression from spin liquid to spin glass to long-range-ordered magnet.

FY 2014 HIGHLIGHTS

One of the key aspects of optimization is the process by which the computer settles into a solution to questions akin to the traveling salesman problem. The solutions exist in a landscape where the heights and depths of features are the total distance travelled; the best solution corresponds to the deepest valley. To find the deepest valley, the optimizer hops between valleys either by thermally climbing over barriers or quantum tunneling through them. We looked at the valleys found after thermal and quantum annealing in the quantum magnet, $\text{Li}(\text{Ho},\text{Y})\text{F}_4$. At low temperatures the speed and strength of thermal annealing can be controlled by rods of sapphire connecting the sample to a dilution refrigerator. The quantum annealing can be controlled by means of a magnetic field that sets the rate of quantum tunneling. We found that when the system reaches its final valley via thermal annealing alone it was dramatically different from the state reached when thermal annealing was weakened and quantum annealing was turned on. The Random Field Ising Model (RFIM) is a simple and powerful approach to quantifying the effects of disorder. While it has been studied extensively via theory and simulations and by decades of experiments on antiferromagnets, the difficulty of realizing the RFIM in bulk ferromagnets has limited the ability to interrogate fundamental quantities like hysteresis loops and avalanche dynamics. We begin to fill this gap in our experiments. We studied the domain dynamics of the ferromagnet $\text{Nd}_2\text{Fe}_{14}\text{B}$ in transverse field, a room-temperature realization of the RFIM. The power-law

exponents and scaling forms of Barkhausen noise events as a function of temperature and transverse field demonstrate that the system can be placed into two regimes depending on tunable disorder: a regime where random-field-induced pinning dominates and one where thermal fluctuations dominate. The deep free-energy minima allow for domain-wall oscillations for extended periods of time.

Thermalization of Artificial Spin Ice and Related Frustrated Magnetic Arrays

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Funding: \$174,149 (2014)

PROGRAM SCOPE

This program encompasses experimental and theoretical studies of lithographically fabricated arrays of nanometer-scale single-domain ferromagnetic islands in which the array geometry results in frustration of the magnetostatic interactions between the islands, known as ‘artificial spin ice’. Such geometrical frustration can lead to multiple energetically equivalent configurations for the magnetic moments of the islands and a variety of associated novel collective behavior. These systems are analogs to a class of magnetic materials in which the lattice geometry frustrates interactions between individual atomic moments, and in which a wide range of novel physical phenomena have been recently observed. The advantage to studying lithographically fabricated samples is that they are both designable and resolvable: i.e., we can control all aspects of the array geometry, and we can also observe how individual elements of the arrays behave. In previous work, we have demonstrated that we can fabricate and probe frustrated magnet arrays, including some geometries that are directly analogous to the “spin ice” materials. We have designed frustrated lattices, controlled the strength of interactions by changing the spacing of the islands, and demonstrated that the island magnetic moment orientation is controlled by the inter-island interactions. Current work is focusing on several different aspects of these systems including thermal annealing of these arrays at temperatures above the Curie point of the ferromagnetic permalloy, a technique that allows better access to the low-energy ground state of these many-body systems. Another set of studies is focusing on electrical transport through connected networks based on artificial spin ice geometries.

FY 2014 HIGHLIGHTS

In FY 2014 we capitalized on our development of an annealing protocol for artificial spin ice and the subsequent observation of magnetic charge ordering. Artificial spin ice was introduced to investigate many-body phenomena related to frustration and disorder in a controllable system that could be locally probed. Because of the large magnetic energy scales associated with the magnetic elements in artificial spin ice, it had previously been impossible to thermally anneal artificial spin ice into desired thermodynamic ensembles. Our group demonstrated a method for thermalizing artificial spin ices with square and kagome lattices by heating them above the Curie temperature of the constituent material, leading to moment ordering and effective magnetic charge ordering respectively. In this FY, we applied this technique to artificial spin ice created on the shakti lattice, a structure that does not directly correspond to any known natural magnetic material. On the shakti lattice, none of the near-neighbor interactions are locally frustrated, but instead the lattice topology frustrates the interactions leading to

a high degree of degeneracy. We demonstrate that the shakti system achieves a physical realization of the classic six-vertex model ground state. Furthermore, we observe that the mixed coordination of the shakti lattice leads to crystallization of effective magnetic charges and the screening of magnetic excitations, underscoring the importance of magnetic charge as the relevant degree of freedom in artificial spin ice and opening new possibilities for studies of its dynamics. This work was published in Nature Physics.

Nanostructured Materials: From Superlattices to Quantum Dots

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Funding: \$525,000 (2014-2016)

PROGRAM SCOPE

This project is dedicated to the main issues arising when materials, especially magnetic ones, are nanostructured in one, two and three dimensions. The comprehensive approach combines preparation of nanostructures using thin film (Sputtering and MBE) and lithography (electron beam and self assembly) techniques, characterization using surface analytical, scanning probe microscopy, high-resolution scattering (light, X-ray, synchrotron and neutron) and microscopy techniques and measurement of physical properties (magneto-transport, magnetic and magneto-optical) and modeling of the results. All preparation of unique materials and devices and most structural and physical characterization are performed in the PI's laboratory at UCSD. More sophisticated structural and magnetic studies at the nanoscale are performed in collaboration at several major DOE funded facilities. This project aims to investigate general physical phenomena, including exchange bias, effects of confinement on magnetic properties, a variety of proximity effects in magnetic hybrids, and induced phenomena by the application of external driving forces such as time varying electric and magnetic fields, light and other types of radiation. In all cases, a crucial ingredient is the reduction of complex or highly correlated materials to the nanoscale, where fundamental changes may occur in their physical properties. The studies performed included fluorides, oxides, borides and organics in addition to many combinations of transition metal elements. The battery of instrumentation continues expanding the experimental capabilities at UCSD and elsewhere. More recently experiments at fast time scales have been started to investigate the very unusual dynamics present in many hybrid systems.

FY 2014 HIGHLIGHTS

ACCOMPLISHMENT Using specially engineered hybrid nanostructures we have obtained control of one of the key properties of a magnetic material, the coercivity, without using a magnetic field. This was shown to be a very general phenomenon, appearing in a large variety of hybrid combinations. **IMPLICATIONS** Science: This development allows engineering novel functionalities in hybrid materials by transferring properties of one into another material. We have engineered a unique, hybrid, magnetic-oxide bilayer in which there is a giant (factor of 5!) change in the coercivity in a very narrow (smaller than 10 degrees K) range of temperature. This is unlike any magnetic material known until now. The possibility of using a voltage or a current as the controlling parameter is being currently investigated. Technology: This development shows the road towards the development of new transformer materials,

which can provide large energy savings in the transformation of electrical energy. This development also has important energy saving implications for the field of data storage and energy-assisted writing.

Fundamental Studies of High-Anisotropy Nanomagnets

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Funding: \$200,000 (2014)

PROGRAM SCOPE

The project is focused on artificially structured nanoscale magnets, a key class of materials important in magnetism and nanoscience. The specific focus is on nanometer-length-scale and real-structure control of new or metastable structures as a means of creating materials with high spin polarization, magnetic anisotropy and ordering temperatures. Innovative aspects of the research include synthesis of new magnetic nanostructures with special fabrication techniques. The proposed research consists of three main parts. The first is aimed at preparation and properties of complex nanoscale clusters and particles where anisotropic structures and surface effects are expected to lead to novel magnetic properties. Both rare-earth-free and rare-earth-containing Co- and Mn-rich systems are explored. The second part is focused on assembly and interfacial interactions in nanoscale composites. Here, the goals are to understand and control the alignment, assembly and coercivity of Co-based two-phase structures where grain size and interfacial exchange interactions are critical. The third part is aimed at exploring new high-anisotropy structures expected to have relatively high Curie temperatures and controllable spin polarizations. The focus is on Mn-based compounds with properties potentially useful for future magnetoelectronic devices. The research is based on a continuing collaboration between groups at the Universities of Nebraska and Delaware. A broad set of experiments is performed over a wide temperature range. These include structural characterization by x-ray diffraction, analytical and high-resolution electron microscopy, Lorentz microscopy and others. Magnetic measurements include dc magnetization to fields of 7 T between 4.2 and 1000 K. The results are correlated with theoretical work on analytical and simulational nanomagnetism to study spin polarization, magnetic nanostructures, anisotropies, magnetic interactions, and magnetization reversal mechanisms.

FY 2014 HIGHLIGHTS

Collaborative experimental and theoretical research has led to two papers highlighting the understanding and control of nanoscale structures to achieve enhanced magnetic properties. In the first, [Adv. Funct. Mater. 23, 3262 (2013)], single-crystal SmCo₅ nanoparticles with an average size of 3.5 nm have been produced by cluster-beam deposition. When closely packed, the nanoparticles showed a super-paramagnetic behavior with a blocking temperature of 145 K. Dispersion of the SmCo₅ nanoparticles in a carbon matrix resulted in increase in both the coercivity and the blocking temperature. Room temperature coercivities as high as 12 kOe have been obtained for the first time in mono-layers of SmCo₅ nanoparticles dispersed in C matrix. δM plots showed that the interactions in the sample with closed packed particles are of exchange type, which could decrease the overall effective anisotropy and coercivity. Coercivity is found to be inversely proportional to the packing density of the

particles. In the second paper [Sci. Reports 4, 6265 (2014)], we have studied magnetic nanomaterials with a view towards new high-performance permanent magnets. The nanostructures are designed from Co- and Fe-rich building blocks without critical rare-earth elements, and often are required to exhibit high coercivity and magnetization at elevated temperatures to 180°C for many important applications. Here we achieve this goal in exchange-coupled hard-soft composite films by effective nanostructuring of high-anisotropy HfCo₇ nanoparticles with a high-magnetization Fe₆₅Co₃₅ phase. An analysis based on a model structure shows that the soft-phase addition improves the performance of the hard-magnetic material by mitigating Brown's paradox in magnetism.

Magneto-Transport in GaAs Two-Dimensional Hole Systems

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Funding: \$175,000 (2014)

PROGRAM SCOPE

Two-dimensional (2D) carrier systems confined to modulation-doped semiconductor hetero-structures provide a nearly ideal testing ground for exploring new physical phenomena. At low temperatures and in the presence of a strong magnetic field, these systems exhibit fascinating, often unexpected, many-body states, arising from the strong electron-electron interaction. Examples include the fractional quantum Hall liquid, the Wigner solid, and the newly discovered striped and bubble phases in the higher Landau levels. Much of the work on clean 2D systems has been performed on 2D electrons confined to a remotely-doped GaAs quantum well. The goal of our DOE project is to study the materials science and physics of 2D holes confined to such wells. Compared to the 2D electrons in GaAs, the 2D holes possess a more complex energy band structure which not only depends on the quantum well width and 2D hole density, but it can also be tuned via perpendicular electric field (gate bias), parallel magnetic field, and strain. These characteristics add new twists and allow for insight into fundamental phenomena in confined, low-disorder carrier systems. In our project we study 2D hole samples, grown via state-of-the-art molecular beam epitaxy, and use low-temperature magneto-transport measurements to explore their novel physics. Among the problems we are addressing are the shapes of Fermi contours of 2D holes and of flux-hole composite Fermions in the presence of applied parallel magnetic field and/or strain. Also of interest are the fractional quantum Hall states, including the state at the even-denominator filling $\nu = 1/2$, in 2D hole systems confined to wide GaAs quantum wells. We collaborate closely with Prof. Roland Winkler (Univ. of Northern Illinois), who is an expert in calculating the energy band in 2D hole systems, and Dr. Loren Pfeiffer who is a world expert in molecular beam epitaxy.

FY 2014 HIGHLIGHTS

When electrons at sufficiently high density are confined to a high-quality wide GaAs quantum-well, they occupy two electric subbands and possess a bilayer-like charge distribution. Under appropriate conditions, the additional layer and/or subband degree of freedom stabilizes a special fractional quantum Hall state (FQHS) at the even-denominator Landau level filling factor $\nu = 1/2$. This state is generally believed to be the two-component, Halperin-Laughlin (Ψ_{331}) state, a FQHS with strong inter-layer and intra-layer correlations. Although the $\nu = 1/2$ state was discovered over 20 years ago, its

observation was only reported in high quality GaAs electron systems until now. During the last year, we made the first observation of the $\nu = 1/2$ FQHS in GaAs hole systems. The evolution of this $\nu = 1/2$ FQHS as a function of hole density in the quantum well is quite unexpected and qualitatively different from what is seen in 2D electron systems. In our study, we also observe an unusual crossing of the two, lowest-energy, hole Landau levels as we tune the 2D hole density. The crossing leads to a weakening or disappearance of the commonly seen odd-denominator FQHSs in the filling range $1/3 \leq \nu \leq 2/3$. But, surprisingly, a new FQHS at the even-denominator filling $\nu = 1/2$ comes to life at the crossing. We tentatively interpret this $\nu = 1/2$ FQHS as a two-component Ψ_{331} state. A detailed understanding of its origin and properties await future research.

EARLY CAREER: Dynamics of Emergent Crystallinity in Photonic Quantum Materials

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Funding: \$150,000 (2014)

PROGRAM SCOPE

The objective of this work is to realize a wholly new platform for studying quantum manybody dynamics, and employ it to investigate physics in the neighborhood of superfluid-crystalline phase transition. This system will be composed of 2D, effectively massive optical-resonator photons, whose interactions are mediated by virtual rydberg excitations. To achieve this, the first ~ 2 years of the effort is being spent to realize the new, strongly interacting, low-decoherence 'photonic material samples,' and the remainder of the effort to employ the unique tools available for manipulating resonator photons to study the behaviours of these samples, focusing in particular on quantum defects in small crystalline systems, and blockade-enhanced approach to driven equilibrium in the system near the phase transition.

FY 2014 HIGHLIGHTS

This year we have succeeded in building the experimental apparatus; we have prepared a laser cooled rubidium gas, loaded it into an optical trap and conveyor belt, and demonstrated transport. We have prepared a medium finesse, degenerate, small-waist optical resonator and installed it in our vacuum system. We have prepared a high-finesse ultrastable resonator, and succeeded in tunably locking our 780nm probe laser and 480nm dressing laser to it. We are now preparing to load the atoms into the optical resonator, and determine the residual electromagnetically induced transparency (EIT) linewidth in the presence of nearby metal surfaces/trapped adsorbed dipoles; as long as this linewidth is well below a MHz, our 'samples' will be ready for analysis, and the target science will begin.

Magneto-optical Study of Correlated Electron Materials in High Magnetic Fields

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Funding: \$484,655 (2014-2016)

PROGRAM SCOPE

Probing energy, symmetry and dispersion of low-lying excitations and studying many-body effects in novel electronic materials via magneto-optical spectroscopy is a longstanding goal of this program. The remarkable properties of graphene have generated a great interest in other inorganic, two-dimensional crystalline materials or Dirac-like surface-state materials with potentially unique electronic and optical properties. Among those 'graphene-inspired' materials, two-dimensional topological insulators and transition metal dichalcogenides are of great interest due to their extraordinary range of new properties and new functionalities. Here, we exploit the exceptional sensitivity and selectivity of optical spectroscopy probes in exploring electronic structure of solids subjected to a strong magnetic field. The proposed work is focused on investigating the optical properties of graphene and its nano-structures, two-dimensional topological insulators and atomically-thin transition metal dichalcogenides, using a combination of various optical techniques with very high magnetic fields.

FY 2014 HIGHLIGHTS

(1) Magnetic field tunable Dirac plasmons in topological insulator (Bi_2Se_3) micro-ribbons. Topological insulators represent an exciting new state of quantum matter exhibiting great potential to revolutionize electronics. In this program, we demonstrate that plasmons can be confined in topological insulator micro-ribbons, and in the presence of magnetic field it couples with the cyclotron motion of Dirac electrons, forming the so-called upper hybrid mode. The resonance frequency of this mode is in the terahertz spectral range, and it can be tuned by varying the external magnetic field. We extract the effective mass of Dirac electrons in Bi_2Se_3 that is consistent with direct cyclotron resonance measurement of unpatterned thin films. (2) Infrared magneto-spectroscopy study of two-dimensional topological insulators. Recently, inverted InAs/GaSb quantum well bilayers have been theoretically predicted and experimentally confirmed as a quantum spin Hall insulator (a two-dimensional topological insulator). In this program, by changing the relative thickness of each quantum well layer, we are able to band-engineer the material from the normal region to the inverted region (quantum spin Hall region) through a phase transition (critical region). We show that in the normal and critical region only single cyclotron resonance can be observed, while in the inverted region multiple cyclotron resonances, as well as anti-crossing behavior, occur. Our observations agree with predictions of eight-band k.p calculation.

Spin-Polarized Scanning Tunneling Microscopy Studies of Nanoscale Magnetic and Spintronic Nitride Systems

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Funding: \$180,000 (2014)

Jointly funded by "Electron and Scanning Probe Microscopies" and "Experimental Condensed Matter Physics"

PROGRAM SCOPE

Taking advantage of electron spins in gallium nitride (a Nobel prize-winning technology) is desirable in order to develop its even greater potential as a spintronic material. This project seeks to investigate spin properties in nitride-based material systems down to ultimately small spatial length scales (such as atomic dimensions), using the advanced technique of spin-polarized scanning tunneling microscopy (SP-STM). Using this method, it is possible to obtain information directly about the polarized and unpolarized spin densities of states at surfaces. We have shown through publications the promising spin properties occurring in nitride systems, such as: manganese, manganese gallium, and iron layers deposited onto semiconducting gallium nitride; manganese and chromium doped gallium nitride layers; and layers of pure manganese and chromium nitrides. We synthesize ultra-thin films of these systems using molecular beam epitaxy (MBE), allowing us to tailor the spin properties with atomic layer precision. The magnetic/spintronic systems are then explored using both STM and SP-STM in which a magnetically functionalized needle-sharp probe is brought to within just a few atomic diameters away from, and then scanned across, the sample surface. Structural, electronic, and spin magnetic properties can be directly obtained as topographical, electronic conductance, and spin conductance images (dI/dV maps), respectively. Correlations among these interrelated properties are provided as the images are simultaneously acquired pixel by pixel. By manipulating tip and sample magnetization using an applied magnetic field, it is possible to deduce 3-dimensional spin information for complex material structures. Such information is also combined with results from different complimentary experimental techniques, and with theoretical calculations as well, in order to address a wide range of fascinating phenomena related to the growth and properties of these materials.

FY 2014 HIGHLIGHTS

Highlights related to the stated program scope include first of all, our work on manganese gallium ultra-thin films (1-25 nanometers) grown on Ga-polar GaN, which was recently published in Applied Physics Letters. We have shown that for the case of slightly Mn-rich growth conditions that there are predominantly three surface reconstruction patterns occurring, including 1x2, 2x2, and 2x3. The most commonly seen 2x2 corresponds to a manganese rich surface having a 3:1 Mn:Ga ratio, in agreement with theoretical calculations; whereas, the film is overall stoichiometric (having a 1:1 Mn:Ga ratio), indicating that excess Mn tends to segregate to the surface of the growing film. Ongoing work is extending to the gallium-rich side of growth, which will ultimately allow a comprehensive understanding of these important magnetic alloys. Secondly, we highlight our discovery of a novel 6x6-patterned surface structure induced by sub-monolayer iron deposition on the atomically smooth, Ga-polar GaN surface. These highly periodic 6x6 structures decorate the surface step edges. First principles calculations find a Ga dimer model consisting of 2/9 monolayers of iron embedded within 7/3 monolayers of Ga, resulting in a relaxed but distorted structure. These results have been published in Applied Physics Letters. Further extension of this work to the N-polar GaN case has also been carried out, which results in completely different structures forming. A final highlight of our recent work is our publication in Review of Scientific Instruments demonstrating the design and capabilities of our low-temperature SP-STM/MBE facility which also includes pulsed laser deposition. This system enables the growth of a wide variety of spintronic materials and their investigation down to the atomic scale under variable magnetic fields at low temperatures. Initial results on the N-polar GaN surface reveal novel features not previously observed in any room-temperature STM images.

Understanding and Controlling Conductivity Transitions in Correlated Solids: Spectroscopic Studies of Electronic Structure in Vanadates

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Funding: \$515,000 (2014-2016)

PROGRAM SCOPE

The scientific and technological interest in solid state conductivity transitions is enormous. The switching of the electrical properties of a material between those of a metal and those of a non-metal is the very basis of the electronics industry. These transitions are also the focus of significant fundamental physical interest. Indeed a substantial fraction of all research in solid state physics is directed at understanding such transitions in some form. Vanadium oxides are a class of solid that displays particularly complex and fascinating properties. Whether as simple binary oxides or as ternary compounds with another metal cation, these oxides are replete with complex conductivity transitions, as well as charge ordering transitions, structural phase transitions, frustrated spin structures, superconductivity, and unusual magnetic properties. Key to understanding the origin of all these phenomena in the vanadates is accurate experimental determination of the underlying electronic structure. This program aims to make definitive spectroscopic measurements of the electronic properties of vanadium oxides, in particular pure and doped VO_2 and V_2O_3 . The primary goal is to use the knowledge gained on the electronic structure of these vanadates to facilitate a deeper understanding of the origins of conductivity transitions in correlated materials. The experimental tools used are soft x-ray emission spectroscopy, soft x-ray absorption spectroscopy, resonant inelastic soft x-ray scattering, x-ray photoemission spectroscopy, angle resolved photoemission spectroscopy, and spectroscopic photoemission low energy electron microscopy (SPELEEM). The use of this suite of techniques enables a wide range of oxides to be studied, since we are able to measure electronic structure in electrical conductors and insulators, and samples in crystal, thin film, or powdered form.

FY 2014 HIGHLIGHTS

During the reporting period we completed a series of new vanadate studies, including direct observation of the separation of the structural and electronic components in the metal-insulator transition of VO_2 , and a study of low-energy orbital excitations in NdVO_3 . Ongoing studies, with manuscripts in preparation, include examination of the effects of rare-earth size on the electronic structure of rare-earth orthovanadates (RVO_3), a study of enhanced electron correlations at the surface of $\text{Sr}_x\text{Ca}_{1-x}\text{VO}_3$, a low energy electron diffraction study of the quantitative surface structure and stability of the VO_2 (110) surface across the metal-insulator transition, and, most excitingly, an ARPES study of the Fermi surface of VO_2 .

Understanding Iron Superconductors/Focus on Nodal Behavior

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Funding: \$150,000 (2014)

PROGRAM SCOPE

This project characterizes (primarily via specific heat, electrical resistivity, and magnetic susceptibility) single- and poly-crystalline iron-based superconductors between 0.4 and 300 K in fields between 0 and 14 T. Quality of sample, particularly a low level of magnetic impurities, is important particularly in the magnetic field measurements. Single crystal samples are both grown in-house and obtained via collaboration. Measuring the iron based superconductors as a function of magnetic field down to 0.4 K determines whether the superconducting gap is fully open or whether there are 'nodes' on parts of the Fermi surface where the gap goes to zero, i. e. where there is a finite electronic density of states. Knowing the nodal behavior is important for understanding the symmetry of the superconducting electron pairing and indeed the nature of the superconducting mechanism itself. In addition, this project has a focus on understanding the 20 K superconductivity in some (*a priori*) undoped single crystals of BaFe₂As₂, which should be non-superconducting. Investigation into the effect of water vapor has progressed to exposure to fluorine gas as well as other reactant gaseous species.

FY 2014 HIGHLIGHTS

Using a series of small mass (~5 mg) single crystals of overdoped Ba_{1-x}K_xFe₂As₂ obtained via collaboration, scaling of the specific heat with both field and temperature has been used to find strong evidence for nodal behavior around x=0.88 in the larger of the two gaps present. This work demonstrates a new, powerful technique for tracking the presence or absence of nodal behavior vs composition in a phase diagram, as well as specifying which gap possesses the nodes.

Thermodynamics of Strongly Correlated Fermi Gases

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Funding: \$157,828 (2014)

PROGRAM SCOPE

The purpose of the proposed program is the broad study of the thermodynamic properties of a strongly correlated Fermi gas of ⁶Li atoms. The primary goals are (1) to make measurements away from (rather than on) a collisional (Feshbach) resonance, to understand the properties when the gas is no longer scale-invariant and (2) to explore a new 'relativistic' regime of this unique quantum gas, by using optical fields to control the dispersion relation of the trapped interacting atoms. This novel cold atomic Fermi

gas will be a paradigm for relativistic strongly correlated matter, from graphene to quark-gluon plasmas, and will bring trapped ultra-cold unitary gases a step closer to theoretical treatment by conformal field methods, which are difficult to apply to non-relativistic systems.

FY 2014 HIGHLIGHTS

We are currently testing our new bichromatic lattice laser system, which has been described in our previous reports. This comprises an IPG 30 W 1064 nm fiber laser and a Toptica frequency doubler with an output of 4W at 532 nm. The beams are sent into fiber-optic cables from the laser table to the vacuum chamber, where two combined beams will intersect at an adjustable angle to create two standing waves, one with a period in the micron range and one half as long, enabling continuous tuning of the atomic dispersion for atoms in our CO₂ laser trap. As a warm-up experiment, we will use the 1064 nm lattice and our CO₂ laser trap to create continuously tunable, quasi-two-dimensional potentials, providing a new tool for the study of layered materials. Another new breakthrough has emerged in our studies of expanding Fermi gases: We have determined the local shear viscosity of the resonantly interacting gas as a function of the temperature from nearly the ground state to the high temperature limit. We use methods borrowed from image analysis to invert the raw trap-averaged shear viscosity to extract the local shear viscosity for the first time. The results are directly compared to recent predictions. A paper on this result is in preparation. We have made the first study of the thermodynamics of spin-imbalanced mixtures in a two-dimensional Fermi gas. We observe phase separation and find that 2D-polarons play a central role in the thermodynamics. This work nicely connects our ARO program on strongly interacting Fermi gases in two dimensions to our DOE program on thermodynamics. A paper on this result is in preparation. We have made the first measurement of the trap-averaged shear viscosity as a function of the total entropy of the cloud in the BEC-BCS crossover. A paper on this result is in preparation.

EARLY CAREER: Control Graphene Electronic Structure for Energy Technology

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Funding: \$750,000 (2010-2014)

PROGRAM SCOPE

Graphene, a one-atom thick sheet of carbon, exhibits incredible structural flexibility, electrical transport, and optical responses. And remarkably, the graphene electronic structure can be varied through interlayer coupling, nanoscale patterning, and electrical gating. The objective of this project is to understand and control the electronic structure using a variety approaches and exploit the unique graphene properties for innovative energy technology.

FY 2014 HIGHLIGHTS

(1) Gate-dependent pseudospin mixing in graphene/boron nitride moiré superlattices: In this work, we demonstrate that the unusual moiré superlattice between graphene/BN leads to a spinor potential with unusual hybridization of electron pseudospins, which can be probed directly through infrared

spectroscopy because optical transitions are very sensitive to excited state wavefunctions. This work is published in Nature Physics in 2014. (2) Observation of an intrinsic bandgap and Landau level renormalization in graphene/ boron-nitride heterostructures: In this study we use magneto-optical spectroscopy to determine the Landau level transitions in this system and reveal a bandgap of ~38 meV (440 K). (Nature communications in 2014.) (3) Photoinduced doping in heterostructures of graphene and boron nitride: In this study we demonstrated photoinduced doping in van der Waals heterostructures consisting of graphene and boron nitride layers. (Nature Nanotechnology in 2014.) (4) Giant bandgap renormalization and excitonic effects in a monolayer transition metal dichalcogenide semiconductor: In this work, we observed extraordinarily large exciton binding energy of 0.55 eV for monolayer MoSe₂ on graphene. (Nature Materials in 2014.) (5) Evolution of Interlayer Coupling in Twisted MoS₂ Bilayers: In this work we demonstrated the evolution of interlayer coupling with twist angles in as-grown MoS₂ bilayers. (Nature Communications in 2014.) (6) Ultrafast Charge Transfer in Atomically Thin MoS₂/WS₂ Heterostructures: In this study we reported the first experimental observation of ultrafast charge transfer in photo-excited MoS₂/WS₂ heterostructures using both photoluminescence mapping and femtosecond (fs) pump-probe spectroscopy and observed the hole transfer within 50 fs after optical excitation. (Nature Nanotechnology in 2014.)

Charge Inhomogeneity in Correlated Electronic Systems

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Funding: \$110,000 (2014)

PROGRAM SCOPE

This project explores the basic physics of high temperature superconductivity through the synthesis and measurement of unique materials. High temperature superconductors are produced by making small chemical changes to a simpler parent compound, a process known as doping. A fundamental question we seek to answer is exactly how does doping create a superconductor. Our primary tool is the control of oxygen content as a dopant ion using a variety of techniques. We have been focusing on two systems. The first is an iron-based superconductor. FeTe is a parent compound typically made into a superconductor by the substitution of Se or S for Te. This kind of doping does not change the charge balance as Te, Se and S all have the same valence. We co-discovered that in film form, FeTe can also be made a superconductor through the incorporation of excess oxygen. Oxygen enters as an ion and causes a large change in the charge balance. Thus comparing FeTeO_x with FeTe_{1-y}Se_y should be a good avenue for understanding the role of dopant ions. We are exploring several curious aspects of FeTeO_x, particularly the interplay between the magnetism and superconductivity. These two electronic states robustly coexist in these compounds; a unique feature. The second system is a copper-based high temperature superconductor. La₂CuO₄ is a parent compound typically made superconducting through the substitution of Sr for La. A superconductor can also be made by incorporating excess oxygen, best done with the unusual procedure of using wet electrochemistry. The oxygen ions are highly mobile, leading to several interesting phenomena including electronic phase separation. Magnetic and superconducting states both develop in one material, but spatially separate to exist in different regions. We are exploring the implications of this electronic phase separation and what it implies about a pure superconductor.

FY 2014 HIGHLIGHTS

Our primary activity during FY 2014 was conducting extensive experiments on magnetism in superconducting samples of FeTeO_x . This material is unique in being both strongly magnetic and strongly superconducting. It can only be made in film form, making magnetic studies difficult. We found two avenues for measuring magnetism in these samples. The first is using neutron scattering. Such experiments typically take large samples, while films are by definition small. After several attempts and improvements in the quality of the films, we were able to perform a magnetic neutron scattering study at the NIST neutron center. A second approach was to study magnetism using Mossbauer Spectroscopy in collaboration with David Hinks and Ercan Alp of Argonne National Laboratory. Dr. Hinks provided target materials enriched in the isotope enriched ^{57}Fe which we used to produce appropriate films. We worked with Dr. Alp conduct experiments using both a conventional laboratory source and synchrotron radiation at the Advanced Photon Source. We were able to establish the presence of magnetism in the superconductor and measure basic properties. A combined paper describing magnetism as measured by both techniques is in progress. A second activity was the preparation of a study of potential charge order in superoxygenated $\text{La}_2\text{CuO}_{4+y}$. This superconductor has been shown to exhibit coexistence of magnetism and superconductivity in a single sample, but in spatially separated regions. The magnetic regions have a stripe-like ordering of ion magnetic moments, implying charges should have similar order. That charge order has never been seen, though the proper experiment may never have been performed. We are oxidizing crystals for just such a measurement, a process that takes several months. We also performed an exploratory measurement at the Canadian Light Source and are prepared for a full measurement in FY 2015.

Imaging Electrons in Atomically Layered Materials

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Students: 0 Postdoctoral Fellow(s), 1 Graduate(s), 1 Undergraduate(s)
Funding: \$140,000 (2014)

PROGRAM SCOPE

Objectives and Significance - Graphene is an exciting new material composed of a single atomic layer of carbon atoms in a hexagonal lattice. Its properties are radically different from traditional semiconductors and open the way for new science and applications. Electrons can travel ballistically over distances $\sim 1 \mu\text{m}$, quantum phenomena are unusually strong, and atomic-scale devices are possible. Goals - Our goal is to address two important questions: How do electrons move through a graphene structure? - how do they pass through barriers and bounce off edges? - what are the effects of disorder? How can one make and study atomic-scale graphene structures? - how stable are different atomic configurations? - what are the electronic states? Approach - Our project will combine the expertise of PI Westervelt in imaging electron motion using custom-made cooled scanning probe microscopes (SPMs) with the skill of collaborator Bell in characterizing materials with transmission electron microscopy using the atomic-resolution Zeiss TEM and JEOL STEM in Harvard's Center for Nanoscale Systems. Research Plan - SPM imaging of Electron Flow in QPC structures - Westervelt's lab will image electron flow in graphene hexagonal boron nitride stacked structures with quantum point contacts (QPCs). The sample size ($\sim 100 \text{ nm}$) should permit ballistic flow. We plan a series of

experiments to image the unusual characteristics of electrons in graphene: cyclotron orbits and magnetic focusing, and electron flow in bilayer graphene. Nanosculpting and Imaging Graphene Structures at the Atomic Scale - Experiments in the high resolution STEM and TEM will move toward the atomic scale by using the electron beam to both cut and image graphene structures. The high resolution of these instruments will permit us to study the materials science of newly cut edges and gaps in a graphene sheet.

FY 2014 HIGHLIGHTS

(1) Scanning capacitance microscopy: We successfully designed and implemented a cooled scanning capacitance probe that operates at liquid He temperatures. The conducting tip of a scanned probe microscope (SPM) is held above the nanoscale structure, and an applied sample-to-tip voltage creates an image charge measured by a cooled charge amplifier next to the tip. We have achieved a low noise level (0.13 e/VHz) and high spatial resolution (100 nm), providing a useful tool to image electron charge density in nanoscale devices. (2) Imaging electrons in BN/Graphene/BN stacks: We have begun a collaboration with Philip Kim to image electron motion in high mobility graphene using a G layer stacked between two insulating hexagonal boron nitride (hBN) sheets. Hall-bar samples with two end contacts and two side contacts on each side were fabricated, showing a mobility $> 30,000 \text{ cm}^2/\text{Vs}$. Using these hall-bars, we plan to image magnetic focusing in graphene, similar to experiments on GaAs/AlGaAs 2DEGs by Kathy Aidala in our lab. A voltage applied between a conductive SPM tip and the graphene layer creates a dip in the electron density directly below that deflects electrons away from their initial trajectories, changing the transmission between two electrodes. By associating the conductance with electron transmission through the Landauer formula, we can map the electron flow. This technique could reveal images of the cyclotron orbits that cause magnetic focusing. In another experiment, we plan to image the coherent flow of electrons in hBN-bilayer graphene-hBN stacks with gate-defined QPCs. Electrons in bilayer graphene have a mass, and backscatter like conventional materials. Extending imaging on GaAs/AlGaAs 2DEG samples by Mark Topinka in our lab, we plan to measure changes in the QPC conductance as the tip is scanned above the surface. This approach should image electron flow, as well as interference fringes generated by paths backscattered by the tip.

Investigation of Spin Physics in Semiconductor Nanowires-Based Heterostructures.

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PROGRAM SCOPE

The goal of this DOE project is to study spin dynamics in low-dimensional systems. The original focus of this project was on spin physics in one-dimensional semiconductors. Motivated by the breakthrough in the PI's lab that enabled growth of $\text{Y}_3\text{Fe}_5\text{O}_{12}$ (YIG) epitaxial films of unprecedented quality and the exciting spin pumping results that emerged, in consultation with our DOE program manager, we shifted our focus to dynamically driven pure spin transport in magnetic heterostructures. Spin currents carried by mobile charges in metallic and semiconducting ferromagnetic and nonmagnetic materials have been the central focus of spintronics for the past two decades, while spin transport in insulators is largely

unexplored. Ferromagnetic resonance and thermally driven spin pumping have attracted intense interest in magnon-mediated spin currents, which can propagate in both conducting and insulating ferromagnets and antiferromagnets. Specifically, in this DOE project, we investigate dynamically generated pure spin currents in antiferromagnetic insulators excited by ferromagnetic resonance and thermally driven spin pumping in YIG-based heterostructures by focusing on a series of antiferromagnetic insulators to reveal mechanisms of spin transfer in antiferromagnetic insulators and across interfaces. The results from this effort open a new venue for exploration of spin manipulation in tailored structures composed of ferromagnetic, antiferromagnetic and nonmagnetic materials.

FY 2014 HIGHLIGHTS

In FY 2014, our DOE grant (DE-SC0001304) is a primary support for 2 papers in Physical Review Letters [PRL 113, 097202 (2014); PRL 113, 176601 (2014)], 2 papers in Physical Review B [PRB 90, 140407(R) (2014); PRB 90, 214428 (2014)], 2 invited papers in Journal of Applied Physics [accepted], and 1 paper in Journal of Applied Physics (accepted). In addition, we have one manuscript under review in a high impact journal and 2 manuscripts almost ready for submission under DOE support. These results include: 1) robust spin transport from YIG to Pt across an antiferromagnetic insulator NiO, which strikingly enhances the inverse spin Hall effect (ISHE) signals at thin NiO thicknesses and can transmit spin currents up to 100 nm NiO thickness, demonstrating highly efficient spin transport through an antiferromagnetic insulator; 2) investigation of spin transport by spin pumping measurements on six insulators using YIG/insulator/Pt trilayer structures, including one diamagnet, one paramagnet, and four antiferromagnets, demonstrating the systematic spin transport behavior mediated by magnetic correlations; 3) surprisingly large inverse spin Hall effect in 3d transition metals which reveal systematic variation of spin-orbit coupling with d-orbital filling; 4) study of magnetic damping of confined modes in YIG thin film by ferromagnetic resonance force microscopy, which demonstrates intralayer spin pumping, i.e., angular momentum transfer across a nanoscale field-defined interface; 5) broadly tunable approach to localizing ferromagnetic resonance modes using ferromagnetic resonance force microscopy through experimental and numerical understanding of localized modes in arbitrarily oriented magnetic fields.

Emergent Phenomena in Quantum Hall Systems Far from Equilibrium

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Funding: \$140,000 (2014)

PROGRAM SCOPE

The main goal of this project is to investigate magnetotransport phenomena in semiconductor nanostructures driven away from equilibrium by microwave and sub-THz radiation. Prominent examples of such phenomena include microwave-induced resistance oscillations and radiation-induced zero-resistance states, as well as Hall field-induced resistance oscillations and dc field-induced zero-differential resistance states. Of particular interest is the previously unexplored regime of separated Landau levels and extending studies of non-equilibrium phenomena to material systems other than 2D electrons in GaAs/AlGaAs quantum wells.

FY 2014 HIGHLIGHTS

(1) We have investigated microwave photoresistance in 2D electron system subject to two radiation fields. We have found that at a certain ratio between microwave frequencies, a new, phase-sensitive photoresistance can appear. This photoresistance oscillates with the magnetic field and can be a good fraction of the total photoresistance under typical experimental conditions. [Phys. Rev. B 88, 245409 (2013)]. (2) Microwave-induced resistance oscillations (MIRO) have been extensively studied for more than a decade but, until recently, have remained unique to GaAs/AlGaAs-based 2D electron gases. Recently, we have observed MIRO in a 2D hole gas hosted in Ge/SiGe quantum wells, confirming that MIRO is a universal phenomenon and demonstrating that microwave photoresistance can be utilized to probe the energy spectrum, disorder, and correlation effects of 2D holes in Ge/SiGe quantum wells. [Phys. Rev. B 89, 125401 (2014)]. (3) We have studied magnetotransport in a high-mobility 2D hole gas hosted in a Ge/SiGe quantum well subject to dc electric fields. We have found that under applied dc bias the differential resistivity exhibits a pronounced maximum at a magnetic field which increases linearly with applied current. This maximum was associated with the fundamental peak of Hall field-induced resistance oscillations, which are known to occur in 2D electron gases in GaAs/AlGaAs [Phys. Rev. B 90, 161301(R) (2014)]. (4) We have observed a colossal negative magnetoresistance (MR) effect in a GaAs/AlGaAs quantum well which is manifested by a drop of the resistivity by more than an order of magnitude at low temperatures and at a magnetic field of only 1 kG. In contrast to MR effects reported earlier, this particular MR is not parabolic and persists to much higher in-plane magnetic fields and temperatures. Remarkably, the temperature dependence of the resistivity at 1 kG is linear up to 30 K and appears to coincide with the high-temperature limit of the zero-field resistivity.

DOE National Laboratories

Complexity from Simplicity: Quantum Criticality and Novel Collective Phases in Itinerant Ferromagnets

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Funding: \$533,000 (2014)

PROGRAM SCOPE

Correlations among conduction electrons in metals leads to collective instabilities where charge, spin, and orbitals can be fully or partially ordered, separated at $T=0$ by quantum critical points (QCPs), where quantum fluctuations decide the stabilities of competing ground states. Much needed is an overarching phase diagram that would show how different types of correlations lead to novel ordered phases such as superconductivity, magnetic and orbital order, and charge localization, to provide direction for the discovery of new materials with purpose-built functionality, which are the feedstocks for advancing new technologies for sensor and device applications, as well as energy conversion and distribution applications. This FWP focuses on the explication of the quantum critical fluctuations that accompany these QCPs, which lead to the breakdown of conventional metallic behaviors and to the stabilization of novel ordered states, particularly superconductivity. We focus on new transition-metal based systems where correlations among the d-electrons lead to moment formation and charge localization, and we

will explore new classes of layered and chainlike compounds where low dimensionality enhances quantum fluctuations. We combine a vigorous program of materials synthesis integrated with the characterization of structure, thermal, magnetic, and transport properties to identify new compounds that order at low or vanishing temperatures. Electrical transport, photoemission and optical spectroscopy measurements will probe the evolution of the electronic structure and correlations as the system is compositionally driven through the QCP. We will quantify moment localization in the ordered, quantum critical, and normal metal phases using neutron scattering and magnetic measurements.

FY 2014 HIGHLIGHTS

In FY 2014, we concluded a suite of extremely accurate magnetic, transport, and specific heat measurements in $\text{YFe}_2\text{Al}_{10}$ which demonstrate anomalous divergencies at the lowest temperatures. Muon spin resonance (MuSR) experiments carried out by our collaborators L. Shu (Fudan University) and D. MacLaughlin (Riverside) found no order above 0.02 K. $\text{YFe}_2\text{Al}_{10}$ is a rare system that forms without the use of pressure or composition to provide tuning to the QCP itself. With A. Tsvetik (CMPMSD), we carried out a complete scaling analysis of $\text{YFe}_2\text{Al}_{10}$ that showed hyperscaling is obeyed and mean field behavior is absent, confirming that this system is the first bulk system where quantum critical fluctuations dominate. This finding, published in PNAS, has touched off a flurry of new work. With Igor Zaliznyak (CMPMSD), we carried out inelastic neutron scattering measurements on $\text{YFe}_2\text{Al}_{10}$, showing that the critical scattering associated with the QCP is instead wave vector independent. This local criticality is also completely unprecedented, and is strong evidence that an electronic instability, possibly involving moment formation, accompanies the magnetic QCP. Chris Homes (CMPMSD) has obtained optical evidence for increasing electronic mass at the lowest temperatures, in potential support of this local criticality scenario. Electronic structure calculations via DFT and DMFT are in progress by members of the CMPMSD theory group to assess the importance of electronic correlations. It is clear that $\text{YFe}_2\text{Al}_{10}$ is a very special system that can significantly advance our understanding of quantum criticality. We are also developing new systems that may have related QC properties. We discovered a new compound $\text{CaMn}_2\text{Al}_{10}$, which is isostructural to $\text{YFe}_2\text{Al}_{10}$. Although Hund's rule usually makes Mn-based compounds highly magnetic, very small Mn moments were found in $\text{CaMn}_2\text{Al}_{10}$, indicating its itinerant character. Neutron diffraction measurements found antiferromagnetic (AF) order above 300 K, but $\text{CaMn}_2\text{Al}_{10}$ becomes ferromagnetic (FM) at the lowest temperatures.

Digital Synthesis - A Pathway to Create and Control Novel States of Condensed Matter

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Funding: \$685,000 (2014)

PROGRAM SCOPE

In our program, we seek to create, characterize and understand novel electronic and magnetic states at interfaces of complex oxides. We synthesize 'digital' heterostructures of perovskite complex oxides in single atomic layer-by-layer manner. This allows us to tailor artificial crystals, superlattices and heterostructures comprising a broad range of complex oxides with great precision. The complex oxides host a diverse range of collective states of condensed matter. The richness of observed phenomena in

these materials, which have also presented some of the greatest challenges to our understanding, is due to their strongly interacting degrees of freedom. Tailoring surfaces and interfaces between complex oxides, and even the layering of atoms within a unit cell provide a unique opportunity for new properties to emerge, that are qualitatively different from their bulk constituents. We seek to explore states that occur as a result of artificially broken inversion symmetry, electronic states that arise as a result charge transfer at interfaces, and interfacial collective states that may be tuned by gating with DC and transient electric fields. These include non-collinear magnetic states, charge ordered states, superconductivity at interfaces, multiferroics and novel two-dimensional electron gases. We work with materials that are known to have interesting phases, such as the manganites, nickelates, ferrites, titanates and cuprates, where the atoms have been 're-arranged' in simple ways – for example by layering the cations in a manner such that the effects of disorder have been engineered away, or where global inversion symmetry is broken – to reveal new properties. We create these materials systems using state-of-the-art, ozone-assisted oxide Molecular Beam Epitaxy (MBE) at Argonne, and characterize them using the major DOE facilities for neutron and photon scattering, and at the DOE Nanoscale Science Research Centers.

FY 2014 HIGHLIGHTS

- (1) We have developed a new way to create artificially polar materials out of materials that are non-polar, but have crystal structures with large unit cells and varied cation valences. This allows us to tailor electrostatic forces within a formula unit to create large distortions in bond lengths and to tailor electronic properties. Our initial demonstration was carried out using Ruddlesden-Popper nickelates, and these results have been published in *Advanced Functional Materials* and in *APL Materials* in 2014.
- (2) We have developed a technique to create and detect thermally generated spin currents in patterned structures of oxide films. A paper regarding was published in *Appl. Phys. Lett.* in 2014 where we able to show that spin currents generated from an epitaxial Fe_3O_4 film could be detected using a CoFeB magnetic film, where the Nernst and inverse spin-Hall effect could be clearly separated.
- (3) We were invited to write a review article in *Annual Reviews of Materials Research* on magnetism in oxide heterostructures that was published in 2014. We reviewed the current status and future opportunities in this field.
- (4) We created superlattices of $\text{SrFeO}_3/\text{LaFeO}_3$, where an electron microscopy study revealed an oxygen vacancy induced polar behavior. These findings were published in *Nano Letters* in 2014.
- (5) We were part of a team that designed and commissioned an oxide MBE system on a grazing incidence x-ray scattering beamline at the Advanced Photon Source. This unique tool allows us to probe the structure of a growing film. Our study on nickelate films was published in *Nature Materials* in 2014.
- (6) We are currently in the final stages of commissioning of a new oxide MBE system that combines sputtering with regular MBE. This will enable the synthesis of oxide heterostructures incorporating refractory 4d and 5d transition metals where spin-orbit coupling plays a central role, leading to novel spin and charge transport properties and new collective states.

Complex States, Emergent Phenomena, and Superconductivity in Intermetallic and Metal-Like Compounds

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Funding: \$2,455,000 (2014)

PROGRAM SCOPE

The goal of this FWP is the design, discovery, characterization, understanding and ultimately control over materials with complex and potentially useful properties. In some cases the systems will be designed to ask, and answer, focused, basic questions (e.g. quantum criticality). In other cases the systems will have direct impact on societal needs (improved superconductors, magnets, thermoelectrics).

FY 2014 HIGHLIGHTS

Over the past year the FWP has made significant impact in the broad fields of Fe-based superconductivity, heavy fermion and quantum criticality, local moment magnetism and the development and discovery of new compounds. Of particular note is the discovery of highly anisotropic, single atom magnetism in Fe substituted Li_3N . Our discovery paper, "Giant magnetic anisotropy and tunneling of the magnetization in $\text{Li}_2(\text{Li}_{1-x}\text{Fe}_x)\text{N}$ " was published in Nature Communications and was based on a systematic development of Li-based solutions, Li-N melts in this case, as summarized in an extensive technical growth paper, "Single crystal growth from light, volatile and reactive materials using lithium and calcium flux" also published this fiscal year. These efforts are the results of BES funding to develop a reactive materials growth and characterization capability in our FWP several years ago. During FY 2014 the lab continued its extensive and fruitful collaborations with other Ames Lab FWPs leading to the discovery and characterization of a new family of R-Cd based quasicrystals, the discovery of the ordering wave vector of the quantum critical heavy fermion YbBiPt , ambient pressure measurements of excitations spectrum in the collapsed tetragonal phase of CaFe_2As_2 , and the ultrafast observation of critical nematic fluctuations and giant magnetoelastic coupling in iron pnictides.

Towards a Universal Description of Vortex Matter in Superconductors

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PROGRAM SCOPE

Complex vortex phenomena in oxide high temperature superconductors (HTS) arise from the strong influence of thermal fluctuations, which is a consequence of the small superconducting coherence length (ξ) and the large crystalline anisotropy (γ). On the other hand these fluctuations are the main obstacle for applications; moreover the problem is general and will also occur in any new-discovered superconductor operating at high temperatures. The control of vortex matter for performance

enhancement requires the design of the pinning landscape by nano-engineering of the material disorder at the scale of ξ , a few nm in HTS. Although the HTS vortex behavior contrasts with the simpler physics in conventional superconductors, according to the present understanding there is no sharp boundary between them. However, modern vortex matter models have been developed to describe the oxide HTS, thus it is important to test them in different systems. Our approach is to perform comparative studies on a variety of materials covering a broad spectrum of properties. The new family of iron-based superconductors provides an opportunity to 'bridge the gap' and check the validity of vortex models in a new family of materials with broad ranges of T_c , ξ and γ . On the other hand, the multi-band superconductivity in the Fe-based compounds introduces a new level of complexity, requiring a re-evaluation of the concept of anisotropy in the vortex behavior. We also obtain valuable information from other compounds such as MgB_2 , a chemically simpler two-band superconductor, and borocarbides that exhibit strong interactions of vortices with their magnetic sublattices. Recently we have expanded the scope of our work to include unconventional superconductors, as well as other areas of condensed matter physics such as quantum criticality, magnetic frustration and metamagnetic transitions.

FY 2014 HIGHLIGHTS

(1) We continued exploring vortex pinning and dynamics in all the main families of superconductors contained in our program, including technologically relevant YBCO-based coated conductors, Fe-based single crystals and MgB_2 epitaxial films. A general theme has been the analysis of how the pinning energy and the dynamic regimes are influenced by the relative size of the vortex core and the defects. In some cases the pinning landscape was engineered by chemical introduction of second phase nanoparticles or irradiation. (2) The new 3He probe allowed us to extend the vortex pinning and dynamics studies to the sub-Kelvin regime. We observed surprisingly large flux creep rates in single crystals of the borocarbide superconductor $ErNi_2B_2C$ ($T_c \sim 11K$). We observed clear anomalies in the creep rate (S) at the antiferromagnetic transition ($T_N \sim 6.3K$), a weak ferromagnetic transition ($T_{WFM} \sim 2.2K$), and another one, whose origin is still unidentified, at $T \sim 0.8K$. To our knowledge, this is the first observation of the effects of magnetic transitions on the vortex dynamics in superconductors. Preliminary results were presented at the 2014 March Meeting of the American Physical Society. (3) Collaborations have been initiated with other BES-MSE projects at LANL, resulting in several nascent research directions. These new research directions include: • "Magnetic ordering in the frustrated J1-J2 Ising chain candidate $BaNd_2O_4$ ". • "Quantum critical exponents in $UCo_{0.77}Fe_{0.23}Ge$ ". • "Double metamagnetic phase transition in $Sr_4Ru_3O_{10}$ ".

Correlated Materials - Synthesis and Physical Properties

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Funding: \$1,630,000 (2014)

PROGRAM SCOPE

The overarching goal of this FWP is to understand, and ultimately control, emergent behavior in strongly correlated quantum materials. Our research combines synthesis, measurement and theory to coherently address questions at the heart of these issues. Our experiments emphasize novel techniques that reveal important quantities and effects, such as time reversal symmetry breaking, nematic susceptibility, the local density of states, and local variation in the current distribution. During FY 2014 our effort has been largely directed towards theoretical and experimental studies of broken symmetry states in cuprate and ferro-pnictide high-temperature superconductors, in the heavy fermion superconductors UPt_3 and URu_2Si_2 , and imaging of edge currents in topological insulators and quantum Hall systems.

FY 2014 HIGHLIGHTS

(1) Quantum criticality in $BaFe_2(As_{1-x}P_x)_2$, (Nature Physics 10, 194–197 (2014)). Quantum critical behavior was observed near optimal doping in the representative Fe-based superconductor $BaFe_2(As_{1-x}P_x)_2$ via measurement of the power law behavior of the electrical resistivity. These measurements establish that the physics of quantum criticality is likely important in determining the physical properties of the Fe pnictides close to optimal doping, possibly including the occurrence of high-temperature superconductivity. (2) Effect of disorder on the resistivity anisotropy near the electronic nematic phase transition in pure and electron-doped $BaFe_2As_2$, (Phys. Rev. Lett. 112, 227001 (2014)). We show that the strain-induced resistivity anisotropy in the tetragonal state of the representative underdoped Fe-arsenides $BaFe_2As_2$, $Ba(Fe_{1-x}Co_x)_2As_2$ and $Ba(Fe_{1-x}Ni_x)_2As_2$ is independent of disorder over a wide range of defect and impurity concentrations. This result demonstrates that the anisotropy in the in-plane resistivity in the paramagnetic orthorhombic state of this material is not due to elastic scattering from anisotropic defects, and is most easily understood in terms of an intrinsic anisotropy in the electronic structure. (3) Evidence of Chiral Order in the Charge-Ordered Phase of Superconducting $La_{1.875}Ba_{0.125}CuO_4$ Single Crystals Using Polar Kerr-Effect Measurements, (Phys. Rev. Lett. 112, 047003 (2014)). High resolution polar Kerr effect (PKE) measurements were performed on $La_{1.875}Ba_{0.125}CuO_4$ single crystals revealing that a finite Kerr signal is measured below an onset temperature- T_K that coincides with charge ordering transition temperature T_{CO} . We further show that the sign of the Kerr signal cannot be trained with magnetic field, is found to be the same of opposite sides of the same crystal, and is odd with respect to strain in the diagonal direction of the unit cell.

Science of 100 Tesla

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Funding: \$809,000 (2014)

PROGRAM SCOPE

This project concerns a coordinated research plan at the extremes of non-destructive high magnetic field, tackling pressing questions in condensed matter physics relevant to the BES mission that only magnetic fields around 100 tesla can answer. Our scientific team ensures that the record delivery of non-destructive magnetic fields reaching 100 tesla provided by the National High Magnetic Field Laboratory is matched by an experimental program in the extremes of high magnetic field that is unparalleled by that any other laboratory – routinely publishing scientific results in fields extending to 100 tesla. Our scientific team is continuously in the process of expanding the variety of physical phenomena that can be accessed by 100 tesla fields, which is enabled by our expertise in key areas of condensed matter physics in strong magnetic fields and extensive international collaborations. Magnetic fields manipulate matter either through a tunable nanometer length scales or a tunable magnetic energy scales (or sometimes both), enabling a great variety of different physical effects to be studied. The magnetic length scale is important for pairing and cyclotron motion in unconventional superconducting materials, which constitutes one of our foremost research focus areas in 100 tesla magnetic fields. The magnetic energy scale is most relevant for tuning competing interactions or phase transitions in multifunctional magnetic materials, which is a second focus area. The magnetic length scale can further be used for tuning commensurability phenomena in low dimensional materials, which constitutes a third focus area of this project.

FY 2014 HIGHLIGHTS

(1) Angle-dependent measurements of the quantum oscillation in underdoped $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$, where $x=0.56$, together with fits to a simple Fermi surface model developed by us in previous papers, have enabled a determination of the Fermi surface of the normal state of the underdoped regime. (2) Measurements have also been made to magnetic fields of 92 T of magnetic quantum oscillations in $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$, up to 15% hole doping. Quantum oscillations are now observed over most of the underdoped regime, indicating them to be a universal property of the pseudogap regime. (3) Angle-dependent magnetoresistance measurements have also been performed on $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ where $x=0.59$, in pulsed magnetic fields of up to 65 T and DC fields of up to 45 T, indicating Fermi surface likely consists of two components. (4) Comprehensive doping-dependent high magnetic field transport measurements on the iron-based superconducting compound $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$, revealing evidence for a quantum critical point near optimal doping (analogous to that believed to exist in the cuprates). (5) Measurements of several insulating iridate compounds have revealed the existence of an extraordinarily large coercive magnetic field. These systems are typically ferromagnetic and exhibit magnetization avalanche phenomena (i.e. magnetization jumps) in swept magnetic fields. (6) Measurements of CeRhIn_5 in fields extending to 92 T reveal features that suggest a possible connection with field-induced charge-density wave phases. (7) A study has also been made of URu_2Si_2 samples prepared using FIB lithography in magnetic fields extending to 45 T. A significant change in the Fermi surface topology is observed to occur at 40 tesla, indicating a localization of the 5f electrons in high magnetic fields. (8) In $\text{SrCu}_2(\text{BO}_3)_2$, we found evidence of a non-negligible magnetoelastic coupling using pulsed magnetostriction measurements. (9) In semimetallic graphite, we performed angle-resolved measurements of the phase diagram and resistivity at high fields.

Magnetic Thin Films

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Funding: \$1,929,000 (2014)

PROGRAM SCOPE

The Magnetic Films Group creates, explores and derives new insights into novel fundamental physics and new materials related to magnetic phenomena. Towards this end we synthesize a variety of thin film heterostructures and more complex lithographically patterned device concepts with the goal to understand and control their physical, chemical and metallurgical properties. We focus especially on emerging new phenomena associated with the competition between spatial and magnetic length scales, as well as proximity effects. Our vision is to understand the ultimate limits of miniaturization and prepare magnetic materials with specifically designed functionalities. Thus we tailor properties via systematic control of preparation conditions and manipulate dimensionalities and geometric confinement by means of thin film deposition via sputtering and electron-beam evaporation combined with advanced patterning and templating techniques. Additional complexity comes from coupled heterostructures, which integrate ferromagnets, antiferromagnets, superconductors, and insulators. Cutting-edge characterizations include the use of neutron-, synchrotron-, and electron-scattering and microscopy at DOE user facilities, as well as sophisticated in-house magnetotransport measurements, low-temperature high-magnetic-field magnetic force microscopy, broadband ferromagnetic resonance, and spatially resolved Brillouin light scattering microscopy. This infrastructure enables us to comprehensively investigate magnetization dynamics, magneto-transport phenomena, and interfacial coupling effects. These new phenomena push the boundaries of fundamental understanding of nanostructured magnetic materials and underlie novel applications ranging from information technologies to energy conversion.

FY 2014 HIGHLIGHTS

- Demonstrated controlled manipulation of spin wave propagation via local Oersted magnetic fields. This enables new approaches for computation with the spin degree of freedom.
- Validated spin Hall spin pumping experiments through the magnetic field orientation dependence.
- Experimentally and theoretically showed how magnetic proximity effects can give rise to reduced spin Hall effects in Pd and Pt. Furthermore identified additional magnetic damping in yttrium iron garnet/Pt bilayers, indicative of magnetic proximity effects.
- Determined spin Hall effects in metallic antiferromagnets and observed systematic trend of increased spin Hall effects for heavier elements, which is also validated by *ab initio* calculations.
- Observed spin transfer torque ferromagnetic resonance in permalloy/MoS₂ bilayers.
- Detected new magnetization reversal mode in exchange coupled antiferromagnetic/ferromagnetic vortex structures.
- Validated the approach of generating antivortices in elongated magnetic elements via dynamic resonant spin ordering.
- Systematically explored the energy transfer in dynamically coupled vortices. Surprisingly, for anti-parallel vortex polarities, applied field always result in a softening of the dynamics.
- Prepared ferromagnetic/superconducting heterostructures with perpendicular magnetic anisotropy. The interplay between magnetic stripe domains and superconducting vortices, resulted in the formation of spontaneous vortex-antivortex pairs and re-entrant superconductivity.
- Analyzed the magnetization reversal process in different composite magnet morphologies, revealing that soft-cylinders-in-hard-matrix gives rise to a maximum energy product.
- Installed new electron-beam lithography system.

Atomic Engineering Oxide Heterostructures: Materials by Design

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Funding: \$727,000 (2014)

PROGRAM SCOPE

A central aim of modern materials research is the control of materials and their interfaces to atomic dimensions. In the search for emergent phenomena and ever greater functionality in devices, transition metal oxides have enormous potential. They host a vast array of properties, such as orbital ordering, unconventional superconductivity, magnetism, and ferroelectricity, as well as (quantum) phase transitions and couplings between these states. Our broad objective is to develop the science and technology arising at interfaces between these novel materials. Using atomic scale growth techniques we explore the synthesis and properties of novel interface phases. Magnetotransport, x-ray, and scanning probes are used to determine the static and dynamic electronic and magnetic structure. Heterostructures with low-density superconductors are developed to explore new regimes of low-dimensional superconductivity, particularly in the presence of tunable spin-orbit coupling. Surface and interface couplings are used to engineer band alignments and control their physical properties. The experimental efforts are guided and analyzed theoretically, particularly with respect to x-ray scattering, superconductivity, and new states of emergent order. A wide set of tools, from analytic field theory methods to exact computational treatments, are applied towards rational heterostructure design.

FY 2014 HIGHLIGHTS

- Bilayer superconducting heterostructures based on delta-doped SrTiO_3 have been systematically investigated both experimentally and theoretically. In terms of the angular variation of the upper critical field, systematic coupling between the superconductors has been observed, from the decoupled limit at wide separations, to increasing coupling on the length scale of the superconducting coherence length. We investigated the role of multiple subband degrees of freedom and interlayer pair tunneling on the transition temperature. Furthermore, by moving to lower density higher mobility samples, we can observe well-defined quantum oscillations in the magnetoresistance, by which we can extract the coupling of the normal state and directly compare to the superconducting state. This suggests a novel approach to designing multicomponent superconductivity using subband structure in quantum wells.
- We developed new scaling theories of non-Fermi liquid metals. These theories are based on a proper renormalization group theory of interacting fermions near a quantum phase transition. Our theory predicts new patterns of universal properties such as the heat capacity behaving logarithmically in temperature in 3 dimensions. It also suggests that near a nematic quantum critical point, there is a significant tendency towards high temperature superconductivity.
- Several investigations of the unconventional state at the $\text{LaAlO}_3/\text{SrTiO}_3$ interface have been performed. By using top-gating, or surface charge/adsorbate control, a new regime of low-density high-mobility electrons can be achieved. Most notably, we see the development of Hall plateau features in a regime of occupying a single light

and single heavy subband. We also measured the gate-bias dependent band alignment, especially the confining potential profile, at the conducting $\text{LaAlO}_3/\text{SrTiO}_3$ heterointerface using soft and hard x-ray photoemission spectroscopy.

Electron Spectroscopy

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PROGRAM SCOPE

The Electron Spectroscopy Group's primary focus is on studies of the electronic structure and associated dynamics of condensed matter systems using High-Resolution Photoemission and Infra-Red Spectroscopy or Optical Conductivity. A new capability, laser based ARPES, is currently under construction. The group carries out studies on a range of materials including strongly correlated systems and nano-structured materials. A special emphasis is placed on studies of High T_c superconductors and topological insulators. The group is also actively engaged in planning new facilities associated with NSLS II.

FY 2014 HIGHLIGHTS

$\text{Pb}_{1-x}\text{Sn}_x\text{Se}$ is a material that can be tuned from a trivial insulator to a Topological Crystalline Insulator (TCI). ARPES studies establish the quantum critical point and show that, on the TCI side, a Lifshitz transition can be induced at the material's surface. This transition can be exploited to manipulate transport in film devices. The shift from Fermi liquid (FL) to non-FL behavior and the removal of superconductivity as a result of increasing cobalt doping has been studied in the optical and transport properties of the Fe-based superconductor $\text{Li}(\text{Fe}_{1-x}\text{Co}_x)\text{As}$. The phase diagram indicates that further cobalt doping recovers the FL behavior but superconductivity remains absent. The collapse of the pseudogap on the electron pocket below the magnetic and structural transition in strongly-correlated FeTe results in an anomalous increase in the low-frequency conductivity and plasma frequency associated with the pocket. Proximity-induced superconductivity in Topological Insulators (TI) represents an avenue for observing the elusive Majorana fermions. Cuprates are considered ideal candidates for inducing superconductivity in TIs, but our ARPES studies show that they are extremely inefficient, due to the short c-axis coherence length. The discovery of a huge Magnetoresistance (MR) in WTe_2 questions the current understanding of transport in a magnetic field. ARPES studies show that the Fermi surface in WTe_2 consists of tiny electron and hole pockets of equal size, implying that the large MR emerges from perfect charge compensation. Using ARPES to measure lifetimes and density of states indicates that optimally doped high temperature cuprates represent a nearly perfect liquid as determined by the viscosity/entropy ratio being close to that determined in the quark gluon plasma.

Superconductivity and Magnetism

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PROGRAM SCOPE

This program undertakes experimental and theoretical investigations of novel superconducting and magnetic materials that are important for fundamental physics and applications. It explores novel physical phenomena associated with superconductivity and its interplay with magnetism and determines the origins of these phenomena for eventual novel application of superconductivity. We investigate materials from macroscopic to meso and nanoscale crystals and heterostructures under controlled environments using a wide range of sophisticated thermodynamic and dynamic characterization tools. One grand challenge pursuit is devoted to the thermodynamic studies of the new iron based superconductors, which embody a new opportunity to create an intrinsically isotropic high temperature superconductor. Another grand challenge pursuit is to develop novel strategies for controlling vortex dynamics at high temperatures where conventional core pinning is ineffective by creating magnetic, adaptive and smart vortex pinscapes to tailor the electromagnetic behavior of type II superconductors. In addition, we are also pursuing research into the collective behavior underlying high power THz radiation from synchronized Intrinsic Josephson Junctions in high temperature superconducting meso-crystals - an example of the remarkable properties that can emerge from complex correlations between individual constituents in far from equilibrium meso-scale systems. We maintain leading programs in experiment and theory, with each deriving strong benefit from close mutual cooperation.

FY 2014 HIGHLIGHTS

We made progress in all the research areas listed above. (1) We discovered that the thermodynamic superconducting anisotropy in iron-based superconductors can be reduced by incorporating a low-density of columnar-defects induced by heavy-ion irradiation and developed a model based on the variation of the electron scattering lengths due to defects. (Nat. Commun.); (2) Using our micro-calorimeter, we settled a controversy regarding the 'true' phase transition between the tetragonal high-temperature and orthorhombic low-temperature phases of Fe-based superconductors; (3) We discovered novel stripe domains and first-order phase transition in the vortex matter of anisotropic high-temperature superconductors. (Phys. Rev. Lett); (4) We imaged current filamentation in large $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ mesa structures via luminescent and scanning laser thermal microscopy; (4) Discovered Rayleigh instability of critical superconducting vortex droplets in meso-Pb crystals (Nature Physics). In addition, we developed a low temperature magnetic force microscope (MFM) to operate in a triple-axis vector magnet environment, a Helium-3 Tunnel Diode Magnetometer for penetration depth measurements and a novel low-temperature thermal imaging system for detecting 'hot-spots' in superconductors.

Interfaces in Epitaxial Complex Oxides

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PROGRAM SCOPE

This project aims at addressing the central challenge of understanding, manipulating, and utilizing hetero-interfaces in epitaxial oxide thin films in order to obtain desired functional properties. In particular, we treat not just the layers of materials as the building blocks in complex-oxide heterostructures but regard the interfaces themselves as fundamental constituents in epitaxial assemblies. Specifically, our objectives are (1) to discover new functional properties in epitaxially stabilized oxides, (2) to explore unprecedented approaches and strategies to control the physical properties that emerge at epitaxial interfaces, and (3) to develop a new paradigm for functional oxides with exceptional control over various energy quanta and order parameters, including electrons, ions, orbitals, spins, phonons, etc. A unique combination of experimental approaches is used to underpin the work. Particular emphasis is given to the growth of perovskite oxides and related materials using pulsed-laser epitaxy utilizing real-time monitoring of interface formation and electronic structure evolution by surface x-ray diffraction and ellipsometry, coupled with detailed *in situ* and *ex situ* characterization techniques giving detailed information on crystallographic orientation and structure, electronic and ionic transport, magnetism, ferroelectricity, etc. In addition, microstructural imaging and local spectroscopy, neutron scattering approaches, optical and soft x-ray spectroscopy, and interactions with theory play key roles in all aspects of this work. The resulting enhanced understanding of interface formation, interfacial behaviors, and interfacial effects on complex materials provide unprecedented guidance in the formation of technologically relevant materials for applications such as energy conversion and storage. Thus, the outcome of this approach will lead to new, highly controlled model systems, allowing us to explore the fundamental physics of functional oxides.

FY 2014 HIGHLIGHTS

We developed epitaxial SrCoO_x oxygen sponges that can shed or absorb oxygen in a short time (<1 sec). The oxygen sponges are also found to be good catalysts, which can effectively reduce oxygen at temperatures as low as 200°C. Moreover, a strong anisotropy in oxygen reduction kinetics in epitaxial brownmillerite SrCoO_(2.5) films, which led to a demonstration of a two orders of magnitude improvement in catalytic oxygen reduction, has been discovered. This result demonstrates that controlling the orientation of catalytically functional defects in cathode materials is a useful design strategy in the development of new materials for advanced energy technologies. Based on layer-by-layer growth technique, we also developed a new route to creating transparent conducting oxides (TCOs) based on the dimensional control of conduction pathways in 2D electron gases within an oxide heterostructure. The new TCO has transparency and electron mobility similar to those of the conventional, more expensive indium-tin-oxide and, thus, may be useful for many technological applications requiring

transparent electrodes. In the area of multiferroics, we clearly delineated the different polymorphs that exist (and co-exist) in strained films of BiFeO₃. It has been demonstrated that the phase coexistence between these polymorphs is not only a consequence of epitaxial constraints, but more importantly a prerequisite of the functionality in this multiferroic material. Moreover, in order to expand current *in situ* film growth capabilities to simultaneously probe atomic and electronic structure evolution in real-time, we developed next generation pulsed-laser epitaxy by combining existing surface x-ray diffraction capabilities with hard x-ray photoemission spectroscopy for understanding and controlling the synthesis processes of novel oxide heterostructures.

Emerging Materials

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PROGRAM SCOPE

Emerging Materials takes up BES Grand Challenges of understanding and controlling matter at the atomic and electronic levels by exploring phenomena lying at the intersection of electron correlation and spin-orbit coupling (SOC). Our approach follows along a synthesis-science link, through which integrated materials discovery and materials physics leads to the unveiling and the understanding of these new phenomena. Guided by this principle, we explore novel states of matter that arise from frustration, either due to the physics of spin-orbit coupling and a d⁵ electron configuration (e.g., Kitaev interactions and quantum spin liquids), or from geometric constraints on long-range order (e.g., chiral spin liquids). Our work also directs us to explore an axis leading from 3d to 5d systems. This trajectory leads us (i) to test the current $J_{\text{eff}}=1/2$ model for iridates and more deeply explore magnetic interactions among these spin-orbit coupled entities, (ii) to go beyond $J_{\text{eff}}=1/2$ by doping chemically or electrochemically into a layered d⁵ Mott insulator assembled from $J_{\text{eff}}=1/2$ units, (iii) to create a pathway of diminishing spin-orbit coupling through 4d and 3d transition metal oxide (TMO) analogs. As its name would suggest, Emerging Materials also strives to discover new materials for new phenomena. In this spirit, we have launched floating-zone crystal synthesis at high pressure, targeting the physics of materials that simply cannot be grown from melts at ambient pressure. Here the enhanced fugacity of the process atmosphere moves phase boundaries and solubility limits. Our broad targets are correlated electron systems in nickel, cobalt, and manganese based transition metal oxides.

FY 2014 HIGHLIGHTS

With spin-1/2 moments on a quasi-two-dimensional square lattice, Heisenberg antiferromagnetic coupling, and no orbital degeneracy, Sr₂IrO₄ is considered a model analog to cuprate superconductors. Following this analogy, we used K atoms to donate electrons *in situ* to the surface of cleaved single-crystal Sr₂IrO₄ and then measured the electronic structure using ARPES as a function of K coverage and temperature. Our results indicate that the parallel between Sr₂IrO₄ and cuprates persists in the metallic phase induced by electron doping, and that the 'breaking up' of a Fermi surface into disconnected segments is a general phenomenon of a system containing certain generic characteristics of cuprates. The formation of an arc, as opposed to 'hot spots' at intersections with magnetic zone boundary,

indicates that the correlation strength in Sr_2IrO_4 , which has been under intense debate, is in the intermediate-to-strong coupling regime. Thus, Mott physics and local correlations are essential for understanding of the physics of Sr_2IrO_4 . We conclude that the phenomenology of the Fermi arc must be accountable within a minimal description of the physics of doping a single band, spin-1/2 antiferromagnetic Mott insulator, as shared by Sr_2IrO_4 and cuprates. Their differences in microscopic electronic structures help separate essential features of high temperature superconductors (HTSC) from material-specific features. Importantly, the nature of the charge gap as of Mott insulating (Sr_2IrO_4) or of charge transfer nature (cuprates) seems to have little bearing on the properties discovered in this work.

Quantum Materials

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Funding: \$1,388,000 (2014)

PROGRAM SCOPE

The Quantum Materials program focuses on condensed matter systems in which quantum mechanics plays an especially important role in determining the nature of ordered phases and the transitions that take place between them. In these systems, competing spin, orbital, and lattice interactions yield a multiplicity of nearly degenerate ground states and complex phase diagrams that can be challenging to characterize. The challenges and opportunities presented by this class of materials motivates the overarching goal of the program, to understand, manipulate, and control competing forms of order that arise through interactions shaped by quantum physics. The pace, scale, and complexity of quantum materials research requires a team-oriented, rather than individual PI, approach. The Quantum Materials group exemplifies this approach, combining theoretical and experimental efforts that comprise (i) extensive thin film and bulk crystal fabrication capabilities, (ii) advanced characterization tools including ARPES, ultrafast optical pump/probe, neutron and X-ray scattering, and transport and thermodynamic measurements, (iii) a theory group whose members are leaders in predictive and phenomenological methods. Currently the program is focused on three overlapping themes – high-temperature superconductivity, topological phases of matter, and strong-spin orbit coupling – in cuprate, iron-pnictide, and iridate compounds.

FY 2014 HIGHLIGHTS

Achievements in condensed matter theory Our theory team has made substantial progress in our two thrust areas: unconventional superconductivity and correlated electron systems with large spin-orbit coupling. In the area of superconductivity, we have developed a powerful effective theory that unifies

phenomena in systems where Cooper pairing is driven by antiferromagnetism. This theory accounts for all known electronic instabilities in the Fe-based, Cu-based and some heavy fermion superconductors. In the area of spin-orbit coupled systems we have developed a theory that accounts for the highly unusual noncoplanar spin helices recently discovered in lithium iridates synthesized for the first time by our group. The novel magnetism is shown to result from Kitaev-Heisenberg coupling on a variety of hyperhoneycomb lattices. Growth and characterization of new materials within the QM FWP Our bulk crystal synthesis and measurement team has achieved the first growth and characterization of an harmonic honeycomb iridate, Li_2IrO_3 , in work performed in collaboration with ALS scientists (Michael Martin) and outside collaboration (R. Coldea, Oxford). Measurements performed on high quality single crystals samples have identified the lattice and magnetic structure, revealed anisotropic magnetic susceptibility, and discovered optical properties associated with the unique magnetism. Our thin film synthesis and characterization team has succeeded in the growth of high quality epitaxial iridate films in both perovskite and pyrochlore structures. We have demonstrated experimental control of properties by utilizing both epitaxial and mechanical strain for potential spintronic applications.

Magnetic NanoSystems: Making, Measuring, Modeling, and Manipulation

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PROGRAM SCOPE

This effort is concerned with magnetism as it is manifested and controlled at the nanoscale. The focus ranges from spins at defects (detection, interrogation, control, and exploitation) to the growth and characterization of complex magnetic molecules, magnetic islands on surfaces, and to solids where nanoscale spin degrees of freedom can have profound consequences on bulk properties, as in the FeAs superconductors. There are comprehensive efforts in synthesis, characterization and theory/computation, performed with local as well as international collaborators. The key goals overall are to discover and then interrogate magnetic materials at the nanoscale to gain both fundamental new knowledge, but also to exploit that knowledge. The program engages in basic research to discover new magnetic materials with unique, useful and controllable/tunable properties. A major effort is put to establish novel measurement techniques, such as nitrogen vacancy (NV)-centers in diamond – based magnetometry, magneto-optics, fast optics and four – probe STM – based device capable of measuring the transport properties at the nano- and meso-scales.

FY 2014 HIGHLIGHTS

We have initiated construction of optical magnetometer based on NV centers in diamonds. This “Magnetic nanoScope” will be a non-invasive optical probe of magnetic field with nanometer resolution and nTesla sensitivity. A low-temperature (4.2 K) confocal microscope with scanning AFM-like capabilities has been ordered from the Swiss company Attocube. A postdoc with the knowledge of the technology (Nusran Naufer) has been hired to construct and operate the new setup and a new lab (Wilhelm 115/117) has been dedicated for this project. We explained the development of magnetism with Sr doping of LaCoO_3 , particularly the import of oxygen sites. Very small energy (3.2 meV/Co) difference between two extended (GGA) band state (magnetic and non-magnetic) minima explain ~50 year problems. X-ray absorption spectroscopy and magnetic circular dichroism at the O K-edge find magnetic oxygen states at the Fermi energy, with oxygen hole states increasing with Sr doping. First principles calculations reproduced the experimental results; attributing magnetism on oxygen to hybridization between Co d- and O p-states. The calculated ground state energy is very sensitive to the degree of rhombohedral distortion (Co-O-Co bonding angle). With experimental structure parameters, the ground state is non-magnetic. Dysprosium islands grown on graphene have fcc(111) and not the bulk hcp(0001) structure. Since nanoscale materials can have properties different from bulk, the fcc(111) Dy are expected to behave magnetically and electronically differently than bulk Dy. Ultrafast infrared magneto-optical spectroscopy provided preliminary evidence on photoinduced magnetism in LaCoO_3 with resonant pumping of crystal field excitation ~0.7 eV.

EARLY CAREER: Origin of Superconductivity in Structurally Layered Materials

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PROGRAM SCOPE

The overarching goal of this work is to develop a comprehensive and predictable design for superconductors that link the behavior of the high superconducting transition-temperature in various materials. The general issues in which we are interested include the following: the structural characteristics that cause superconductivity; the effects of various chemical substitutions, pressures and magnetic fields on superconductivity; the development of superconductivity from a normal correlated state; the anisotropic properties of the superconducting and normal states; the identification of the underlying electron pairing mechanism; the nature of the charge carriers and their role in causing superconductivity; and the possible interaction between magnetic ions and superconducting charge carriers. In addition to synthesizing known materials in high-quality single crystal forms for furthering the understanding of physics of superconductivity, we aim at synthesizing new phases by replacing the iron transition-metal element, or arsenic, in iron arsenide based superconductors. The synthesis of materials is accomplished by the use of a variety of advanced solid-state techniques. The physical properties of materials are studied as a function of the concentrations of the chemical constituents and types. Such research should lay a foundation in predicting new superconducting materials with improved properties.

FY 2014 HIGHLIGHTS

Much of our studies probed the nuclear, electronic, and magnetic details of known superconducting materials, in high-quality single crystals, in order to add fundamental knowledge about causes of superconductivity; a few research examples follow. For praseodymium-doped barium-iron-arsenide, we found non-uniform local distortions through isolated praseodymium atoms that prevent percolation path for bulk superconductivity [Phys. Rev. Lett.112 (2014), 047005.]. For calcium-iron-arsenide, we found that a large Fermi-surface reconstruction in the non-magnetic phase causes the non-superconducting ground state [Phys. Rev. Lett. 112 (2014), 186401.]; different crystalline domains with varying lattice parameters were identified for this material [Scientific Reports 4 (2014), 4120.]. For copper-doped barium-iron-arsenide, we found that an orthorhombic distortion below structural transition leads to magnetically ordered state of iron arsenide planes that destroy superconductivity [Phys. Rev. Lett. 113 (2014), 117001.]. In addition, we focused part of our research on understanding superconductivity in materials under applied pressures and reduced lattice sizes; a few research examples follow. Evidence for superconductivity was found in oxygen-deficient molybdenum oxide simple binary [Phys. Rev. B 90 (2014), 054505]. We found pressure-induced superconductivity and structural transitions in ruthenium-doped barium iron arsenide [Eur. Phys. J. B 87 (2014), 68.], while neutron diffraction measurements trace the antiferromagnetic susceptibility under uniaxial pressure [Phys. Rev. B 89 (2014), 214404.].

Correlated and Complex Materials

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PROGRAM SCOPE

The ultimate goal of our research is to attain a predictive understanding of the behavior of correlated and complex materials (CCM). The experimental tools of materials synthesis, compositional tuning, and crystal growth are used to address cutting edge issues in the physics of these systems, with particular focus on the discovery and investigation of novel cooperative phenomena and new forms of order in CCM. Phenomena such as charge and orbital ordering, coupling of magnetism and ferroelectricity, unconventional superconductivity, low carrier density helimagnetism, time dependent magnetization, ferromagnetism, magnon heat conduction, and anharmonic phonons in thermoelectric materials are investigated. A substantial fraction of the effort is devoted to the discovery of innovative materials and the growth of large single crystals of fundamental interest to material physics. The composition of these materials is carefully controlled, and the effects of compositional tuning on the basic physics of the materials are studied using X-ray and neutron diffraction, magnetization, specific heat, and electrical and thermal transport. Once the materials have been prepared and characterized, in-depth experiments such as inelastic neutron scattering, photoemission, and scanning tunneling microscopy are performed

in order to obtain a deeper understanding of the relevant physics. Some of the materials investigated are promising for energy-related applications such as superconductors for grid applications and thermoelectrics and new permanent magnets for energy conversion.

FY 2014 HIGHLIGHTS

- Discovered that BaFe_2As_2 and CaFe_2As_2 are not tetragonal but orthorhombic at room temperature with nanometer sized domains
- Found that size of orthorhombic domains at room temperature in $\text{BaFe}_{(2-x)}\text{Co}_{(x)}\text{As}_2$ correlates with estimated magnitude of dynamic iron magnetic moment, which mimics the magnetic-superconducting phase diagram found at much lower temperatures
- Discovered glassy and time-dependent magnetism in a stoichiometric compound, DyRuAsO , despite no evidence of disorder or frustration
- Grew and characterized the first single crystals of the Dirac material EuMnBi_2
- Discovered large magnetoresistance (600%) in EuMnBi_2 at low temperatures
- Showed that large anharmonicity in PbTe was due to nesting of phonon modes - a result that can be used to help predict new thermoelectric materials
- Grew and characterized high quality single crystals of WSe_2 and MoSe_2
- Showed that metal-insulator transition in Sr_2IrO_4 has a strong Slater character

Photonic Systems

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Funding: \$894,000 (2014)

PROGRAM SCOPE

Since ~1990, the Ames Laboratory has conducted pioneering development and studies of 3D photonic crystals (PCs), developed forefront organic light-emitting diodes (OLEDs) and procedures for characterizing them, and conducted pioneering optically detected magnetic resonance (ODMR) studies on organic semiconductors and OLEDs. PCs, artificial periodic dielectrics or metallic structures, have revolutionized control and manipulation of photons, similar to the control of electrons in semiconductors. Photon diffraction by PCs has opened new vistas to control spontaneous emission, chemical reactions, optical communications, sensing, energy-efficient lighting, displays, and, in particular, solar cells. In parallel, OLEDs and organic electronics are developing rapidly, with particular relevance for solid state lighting. These research areas are combined into four interrelated tasks that will be performed in the next three years. Besides continuing studies in each of these areas, we will use our vast expertise to enhance light emission from OLEDs, thereby combining the PC expertise with (organic) light-emitting structures. We will explore new functionalities of PCs, including lasing and non-linear effects and utilize low-cost methods to design and fabricate large-area PC and OLED structures relevant to energy-related applications. In close relation to ODMR, we will also explore organic spintronics. There will be a close synergy between theory, simulation, fabrication, and experimental studies in these interrelated tasks.

FY 2014 HIGHLIGHTS

We have just demonstrated a top-emitting (small molecule) OLED (TEOLED) with peak luminous efficiency $\eta_L = 217$ candela/A and power efficiency $\eta_p > 200$ lumens/W – among the highest reported to date for any light source (for the incandescent bulb, $\eta_p = 15$ lumens/W). Using high-quality microlens arrays (μ LAs), in collaboration with UCLA Profs Gang Li and Yang Yang, we are obtaining record setting organic solar cell efficiency, which the μ LAs enhance by $\sim 7 - 10\%$. We have simulated the enhancement due to the μ LAs and other surface patterns, which will determine the optimal pattern to enhance organic solar cell efficiency. After previously demonstrating an OLED-based spectrometer-on-a-chip for the 493 – 650 nm, we have expanded this spectrometer to include the near UV-blue bands at 370 – 469 nm. Moreover, we have launched our new effort on organic spintronics. It focuses on the spin relaxation rates of polarons in organic semiconductors in general and in organic magnetic spin valves, i.e., organic FETs (OFETs) with ferromagnetic contacts to the source and drain, in particular. Initial results indicate that spin polarization is enhanced by the applied electric field E_{appl} in the OFET. We derived and demonstrated a simple analytic Q factor model that elucidates the lasing threshold of a PC slab vs interface reflectivities (impedance), group velocity (band structure). It shows how the lasing threshold may be dramatically altered inside a band or, vitally, close to the band edge. Our simple model enables understanding and optimizing the design of PC-based lasing structures. We experimentally and theoretically demonstrated that a 2-layer dielectric structure can collimate and enhance transmission of a Gaussian beam passing through it. This demonstrates that low-loss purely dielectric resonant surface states can be leveraged for low loss beam collimation. A system of multiple cascading bilayers can sustain the beam for large propagation distances.

Electronic Complexity of Epitaxial Rutile Heterostructures

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PROGRAM SCOPE

Complex transition metal oxides exhibit a plethora of fascinating broken symmetry states that emerge from the intricate interplay between the various quantum mechanical degrees of freedom of these materials, including electronic and/or spin excitations, orbital ordering, and cooperative lattice deformation. While most investigations to-date have focused on complex perovskite systems and related heterostructures, rutile heterostructures offer a particularly unique and hitherto unexplored perspective for tuning electronic complexity and emergent properties in complex oxides. In particular, the presence of edge shared MO_6 octahedra (M =metal cation) and formation of direct cation-cation bonds in rutile tends to lower the effective dimensionality of the electronic structure, compared to corner-shared perovskite systems, and greatly facilitates the growth of non-polar (001) and (110)-oriented heterostructures. The existence of two growth orientations, along with the extreme anisotropy of the metal-metal sigma-bonds, offers a unique opportunity to vary the occupation of selected $3d-t_{2g}$ orbitals via quantum confinement, and their coupling to the other degrees of freedom. The investigations aim to understand and tailor the electronic, orbital, and spin degrees of freedom of

quantum-confined rutile heterostructures, and explore the existence of recently-predicted and/or other competing quantum phases for select heterostructures. We pursue a comprehensive and timely approach involving epitaxial synthesis, in-situ electron spectroscopy, and *ab initio* DFT and post-DFT calculations. Fundamental knowledge that will be gleaned from these studies will broaden and deepen our understanding of complexity and spontaneous symmetry breaking in correlated electron systems, and elucidate how collective materials properties can be controlled through manipulation of the electronic and orbital degrees of freedom.

FY 2014 HIGHLIGHTS

In this first year of the project, we designed, built and put into operation an oxide MBE system at ORNL, featuring transition metal sources, and oxygen plasma source, *in situ* electron diffraction, and a laser sample heater allowing for fast and high pressure sample annealing. We have developed a procedure to obtain TiO₂(001) substrate surfaces suitable for subsequent epitaxial growth of rutile films. The TiO₂(001) surface is notoriously difficult to prepare for heterostructure growth, because its high surface energy drives the surface morphology through an irreversible faceting transition that renders the surface unsuitable for subsequent growth. Our results reveal that the atomically flat morphology we obtain even survives after high temperature annealing in vacuum. We used a new method to dope TiO₂ by incorporating Cr-N dopant pairs. Using soft X-ray spectroscopies we elucidated the orbital nature and energy of the dopant-induced gap states, as well as the nature of the charge excitations. Moreover, an extraordinarily large (>1 eV) reduction of the TiO₂ bandgap, in part by delocalized dopant states, was established. We proposed and demonstrated an approach analyzing the speckle patterns formed by visible laser light upon reflection off of a VO₂ film. This approach allowed us to study mesoscopic phase separation associated with the metal-insulator transition of VO₂ with both high time and spatial resolution. Finally, preliminary theoretical results, obtained to benchmark the computational methods used for our heterostructures, indicated unexpectedly that the ground state of bulk RuO₂ is different from the accepted nature of the ground state. We have confirmed these findings with preliminary experimental results.

Novel sp²-Bonded Materials and Related Nanostructures

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Students:	0 Postdoctoral Fellow(s), 3 Graduate(s), 0 Undergraduate(s)
Funding:	\$1,052,000 (2014)

PROGRAM SCOPE

The sp² program studies, both theoretically and experimentally, sp²-bonded structures, which include carbon nanotubes, graphene, nanowires, onions, fullerenes, nanocrystals, hybrid structures, non-carbon

nanomaterials (including BN), and nanococoons. We are interested in the design, synthesis, characterization, and application of sp^2 -bonded materials whose dimensions range from 1-100 nm. This program has three major thrusts: (1) Fundamentals: Focus is placed on theoretical predictions of new stable structures, theoretical and experimental examinations of intrinsic electronic, magnetic, and mechanical responses, transport measurements (electrical resistivity, thermal conductivity, isotope effects, Raman, photoemission spectroscopy, TEM, STM), and mechanical properties and tensile strength. (2) Functionalized nanosystems: where two or more distinct nanostructures are brought together and allowed to interact. Here we focus on methodologies to integrate nanosystems comprised of nanotubes and other nanoparticles interfaced with complementary nanostructures. 3-Directed growth of nanostructures: where novel synthesis methods are explored for non-equilibrium growth of sp^2 -based and other nanoscale materials. This program also seeks to develop specialized instrumentation for synthesis, characterization, and applications.

FY 2014 HIGHLIGHTS

During the past fiscal year the sp^2 program embarked on an ambitious effort to scale-up the synthesis of pure boron nitride nanotubes (BNNTs). Such tubes are formed by sheets of sp^2 -bonded boron and nitrogen in a 1:1 configuration; and are uniform wide-band-gap semiconductors. The bandgap is predicted to be independent of tube diameter or chirality. BNNTs were discovered by LBNL-MSD researchers 20 years ago, but limited production methods have hampered extensive physical properties characterization and application. A new extended pressure, inductively-coupled thermal plasma system was designed and constructed from the ground up for nanomaterials synthesis. In initial trials, the system produced high quality, nearly pure double wall BNNTs at a record rate of 35g/h, using pure boron and nitrogen as precursor materials. For the next period, the BNNTs thus produced will be characterized via optical methods and mechanical methods. They will also be incorporated into membranes and composites for further electronic, magnetic, and thermal fundamental science and applications study. In another sp^2 -sponsored discovery, graphene was mated to 2-dimensional hexagonal boron nitride, and calcium dimers were dispersed on the graphene. A scanning tunneling microscope (STM) was then used to push the dimers together to form artificial atoms of tunable nuclear charge. Nuclear theorists had predicted 70 years ago that ultra-heavy nuclei could cause 'atomic collapse' where the ultrarelativistic electron spirals into the nucleus. It had never before been observed. For the artificial heavy atom living on graphene, STM spectroscopy unambiguously revealed the analogous atomic collapse state. A strong experimental/theoretical collaboration enabled this work. For the next period, the collapsed states will be further characterized as a function of charge, temperature, and underlying/overlying dielectric, dimensionality, and deposited atomic species type.

Materials Chemistry

Institutions Receiving Grants

Fundamental Science of High Open Circuit Voltage Excitonic Solar Cells

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Funding: \$250,000 (2013-2014)

PROGRAM SCOPE

As a counterpoint to the largely Edisonian progress in the vast field of organic photovoltaics, we characterize the morphology of a limited number of high performance bulk-heterojunction devices and materials systems in great detail with novel methods and thus establish improved structure-function relationships and fundamental understanding. Our long term goal is to develop a predictive device paradigm based on understanding of the fundamental interactions and properties of the active materials and the processing solvents and additives used. High performance polymer:fullerene and small molecule:fullerene systems with efficiencies >7% will be investigated. This includes the best small molecule system as well as the materials system that has the best performance for thick films. The detailed understanding of the performance bottlenecks as well as elucidation of the controlling materials aspects of why these systems are the best to date will help facilitate a transition from a “trial and error” approach to a constructionist approach to device design and fabrication. The detailed characterization will be related to fundamental interactions such as the miscibility between the donor and the acceptor material and calculated and measured interaction with the solvents and solvent additives used to cast the active layers. Since most of the time, changes in processing affect a multitude of morphological parameters, these fundamental, thermodynamic quantities will be related to all measured aspects of the morphology determined and not just the overall device performance. Establishing a connection between fundamental properties and device morphology and performance will allow the construction of a predictive device design and fabrication model.

FY 2014 HIGHLIGHTS

Polymer solar cells are a promising renewable energy technology. Development of novel materials and device architecture for further enhancing their efficiency requires fundamental understanding of the impact of chemical structures on photovoltaic properties. Given that device characteristics depend on many parameters, deriving structure-property relationships has been very challenging. We have thus exhaustively studied devices based on fluorinated benzotriazole (FTAZ-a high performance donor) copolymers. In this case, a single parameter, hole mobility, determines the fill factor of several hundred nanometer thick bulk heterojunction photovoltaic devices based on a series of copolymers with varying amount of fluorine substitution. We attribute the steady increase of the hole mobility with the fluorine content to changes in polymer molecular ordering. Importantly, all other parameters, including the efficiency of free charge generation and the coefficient of non-geminate recombination are nearly identical. Our work emphasizes the need to achieve high mobility in combination with strongly

suppressed charge recombination for thick devices required by mass production technologies. The work was published in JACS and highlighted by the editor. We have also been able to achieve record photovoltaic performance in collaboration with the group of H. Yan from HKUST. In this work, aggregation controlled by a specific molecular motif was identified. It allowed for a temperature controlled aggregation during creation of the active layers of a device, and resulted in a robust morphology determined by the donor polymer. Consequently, the devices worked well with a number of different fullerenes, a novel achievement in its own right. The results were published in Nature Communications.

High Efficiency Biomimetic Organic Solar Cells

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Funding: \$300,000 (2014)

PROGRAM SCOPE

Charge transfer states are bound combinations of an electron and hole located on separate molecules. They play a crucial role in organic photovoltaics and organic light emitting devices (OLEDs). In solar cells, charge transfer states mediate both photocurrent generation and recombination losses. In OLEDs, charge transfer states are traditionally the precursors to the light emitting exciton, but they have also been used more recently to directly generate efficient electroluminescence because the two spin configurations can easily mix given the small exchange splitting of most charge transfer states. Our program is a joint theory and experimental study of charge transfer state dynamics, focusing on the key questions of: How big should a charge transfer state be? What is the optimal spacing between the electron and hole that allows it to split efficiently into charge while still being readily formed from a photoexcitation? How do we control the spin of a charge transfer state, and how does its spin determine the light emission, recombination loss, and photocurrent generation properties? And finally, how can we engineer charge transfer states for efficient solid state lighting? In each case, we simulate charge transfer state dynamics and compare to experimental studies in prototype light emitting devices and solar cells.

FY 2014 HIGHLIGHTS

We have three primary results to report this year. First, we examined the question: How big should a charge transfer state be? We measured recombination losses as a function of the electron-hole spacing in fluorescent charge transfer states, including direct monitoring of both singlet and triplet charge transfer state dynamics. Large donor-acceptor separations minimize back transfer from the charge transfer state to a low-lying triplet exciton 'drain' or the ground state. The triplet drain quenches triplet charge transfer states that would otherwise be spin-protected against recombination. Future organic solar cell designs should focus on raising the energy of triplet excitons to better utilize triplet charge transfer mediated photocurrent generation or increasing the donor-acceptor spacing in order to minimize recombination losses. Second, we report the first direct nanoscale imaging of charge transfer states in solar cell donor-acceptor blends. After generation of a charge transfer state, we demonstrate that energy moves geminately over distances of 5-10nm, driven in part by energetic disorder and

diffusion to lower energy sites. Our direct imaging is complemented by magnetic field modulation of the charge transfer state fluorescence that demonstrates that charge transfer states 'breathe' during their diffusion, expanding before ultimately recombining, thereby providing an important method for mixing singlet and triplet states. Third, we report a new mechanism for the efficient generation of light through a charge transfer state in an OLED. We engineer the crystal packing of excimers to give the most efficient charge transfer state emitter reported to date with a peak external efficiency exceeding 8%. Scientifically, the work suggests that crystal packing can be crucial to the fine control of splitting between the emissive singlet and dark triplet configurations of charge transfer states.

Novel Pnictides with d- and f- Metals as Prospective Materials for Thermal Energy Conversion

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PROGRAM SCOPE

Thermoelectric materials allow for the direct inter-conversion of electricity and heat and can be used in power generators, or conversely, in solid-state refrigerators. Such technologies with no moving parts have the potential for widespread applications; however, thermoelectric devices are not part of the everyday life because of their low efficiencies. This, in essence, is a result of the low values of the thermoelectric figure of merit for almost all known materials. Better understanding the relationship among the composition, structure, electronic structure and physical properties is critically needed for the development of improved thermoelectrics. This project seeks to identify new bulk materials for applications in solid-state energy conversion. Using rationally designed syntheses, we have begun thorough and systematic studies focused on the development of the fundamental chemistry and physics of novel intermetallic compounds at the borderline between the typical metals and the typical semiconductors (Zintl phases). The goal of the work is to identify new materials that are based on the metals from the lanthanide series, the transition metals with half-filled or completely filled shells and the heaviest group 15 elements, Sb and Bi. Ultimately, the derived structure-property relationships (established on the basis of experimental work and theoretical investigations) will be used as a solid ground for developing a rationale for the tuning of potentially interesting properties of the newly synthesized materials. These efforts are an integral part of a broad interdisciplinary program to investigate wide variety of lanthanide-based intermetallics with useful magnetic, electronic, and transport properties. Both the thermoelectric and the condensed matter communities at large will directly benefit from the results, which, undoubtedly, will advance not only the research on thermoelectric materials, but also our knowledge in solid-state sciences as a whole.

FY 2014 HIGHLIGHTS

Our prior work had established relationships, which provide some logical and reasonable predictions for possible new compounds in the targeted systems, their likely structures and potential properties. Highlighted below is just one new structural family. A striking observation surveying the structures of the known ternary pnictides is that they are all made up of isolated, edge-shared or corner-shared MPn_4 (M = metal) tetrahedra forming either one-dimensional 1D chains, 2D layers, or 3D frameworks. Such

structural topologies appear amenable to integration of new species. Taking advantage of this flexibility, we explored the possibility of creating more structural complexity in terms of chemical bonding and compositions in a related class of compounds by introducing the smallest alkali metal cation, Li⁺. The first set of quaternary pnictides with formula Ba₄Li₂Cd₃Pn₆ (Pn = P, As, and Sb) feature 1-D infinite chains of [Cd₄Pn₁₀] super-tetrahedral clusters. These chains are connected through Pn₂-dumbbells into corrugated 2-D layers. The adamantane-shaped T₂ is a second member of the series of supertetrahedral T_n cluster (where n is the number of tetrahedra along each edge), which can be viewed as fragments of the cubic ZnS-type lattice. We will also note here that the Ba₄Li₂Cd₃Pn₆ structure appears to be first example of a connectivity mode based on the large [Cd₄Pn₁₀] adamantane-like clusters. The second fascinating feature of the structure is the one-dimensional chain made up of supertetrahedral clusters, connected to each other via common Pn vertexes. Such atomic packing with T₂ cluster makes these materials to be structurally related to a family of layered compounds including In- or Ga-sulfides or selenides. The present work represents a rare case and the first instance of ordered quaternary pnictides built upon adamantane-like clusters assembled into infinite chains. Our studies have helped open a new field with great opportunities for new discoveries.

Low-Temperature Chemical Routes to Functional Complex Oxide Nanocrystals

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Funding: \$450,000 (2014-2017)

PROGRAM SCOPE

Despite over fifty years of developments in the field of materials chemistry, there are still only a limited number of ways to rationally and reproducibly synthesize inorganic materials – the majority of which require harsh reaction conditions. In 2004, a DOE-sponsored Grand Challenge workshop on Nanoscience Research for Energy Needs recommended “developing, understanding, and optimizing synthesis methods for . . . [the] production of nanomaterials” as being a vital nanoscience research theme for energy applications. As such, there is a need to develop general methodologies, using rational chemical design principles, for the synthesis of functional nanomaterials under bench-top conditions. This will enable a “materials by design” approach to be taken, in which new functional nanomaterials can be rationally synthesized for use in next-generation energy applications. To address challenges such as these, more robust and general strategies are needed for the synthesis of high quality complex oxide nanocrystals (with a focus on small size, well-defined composition, and controlled surface chemistry). While there has been a great deal of progress over the past 25 years in the synthesis of high quality II-VI and lead-salt IV-VI semiconductor nanocrystals, there has been much less success in the synthesis of nanocrystals of other materials families, such as complex metal oxide nanocrystals. We will execute basic research in the area of complex oxide nanocrystals that can ultimately impact energy applications with the following three objectives: (1) Leverage the PI’s vapor diffusion sol-gel method to synthesize more compositionally complex oxide nanocrystals. (2) Perform high-level structural characterization of the resulting complex oxide nanocrystals to establish structure-property relationships at the nanoscale. (3) Assess the functionality of the resulting complex oxide nanocrystals.

FY 2014 HIGHLIGHTS

The project start date was September 1, 2014. Thus far, we have successfully extended our vapor diffusion sol-gel method to synthesize well-defined scheelite AWO_4 nanocrystals (where $A = \text{Ca, Sr, Ba}$). Such materials are of interest as host materials for solid-state phosphors, anode materials for Li-ion batteries, and as scintillators. While these alkaline earth tungstates have been previously synthesized under benign conditions using precipitation methods, the resulting material is typically ill defined and microstructured. We can make well-defined nanocrystals under benign conditions (i.e., atmospheric pressure, 100 °C, pH 7), and demonstrated that the resulting sub-30 nm AWO_4 nanocrystals could be compositionally tuned by both facile isovalent and aliovalent substitution using this synthesis method. A thorough local structure study of the as-synthesized scheelite nanocrystals is currently underway using a combination of variable temperature Rietveld and pair distribution function X-ray analysis (APS, Argonne National Laboratory, 11-ID-B). These data are being used to investigate the effect of chemical substitution on the known orientational disorder in these systems in order to probe whether it is static or dynamic in nature.

New Superconducting Materials

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Funding: \$558,000 (2014-2017)

PROGRAM SCOPE

With the goal of discovering new superconductors, this program concentrates on the discovery and chemical, structural and electronic characterization of compounds in three chemical families: ThCr_2Si_2 -type pnictides, tungsten oxide bronzes, and intermetallic compounds with the half-Heusler crystal structure. As a result of previous DOE-sponsored research, the PI has previously found a variety of unusual structure-property relationships that arise in these phases due to the presence of a pnictogen dimer in their crystal structures – in effect, a molecule imbedded inside a metal. Now we are following these relationships for new groups of compounds. The tungsten oxide bronzes were among the first oxide superconductors discovered. They are unusual because they display superconductivity in non-perovskite oxide crystal structures with very low electron counts, with the electrons in orbitals that are derived from tungsten 5d states, which are therefore expected to be broad in energy and relatively uninteresting from an electronic perspective. The PI has developed an understanding of these potential superconductors that suggests that O-W-O bonding with angles other than 180 degrees in their crystal structures can lead to sharper than expected features in their electronic density of states and therefore greater potential for superconductivity. Finally, the half-Heusler crystal structure hosts relatively few superconductors but the ones that do form are very interesting from the perspective of condensed matter physics. We are currently performing a set of studies to try to determine how common superconductivity will be in compounds with this crystal structure, and the primary chemical requirements for the superconductivity when it does occur. All three of these families fall within the PI's general belief that new superconductors can best be found in chemical systems where the bonding cannot be considered as either fully ionic or fully covalent.

FY 2014 HIGHLIGHTS

The superconducting $M_x\text{WO}_3$ tungsten bronzes show several distinct crystal structures. They can have hexagonal bronze (HTB), tetragonal bronze (TTB-I), or perovskite-derived tetragonal (TTB-II) and cubic (CTB) structures. Although the HTBs have been well studied, a detailed investigation of the superconducting properties of the tetragonal tungsten bronze (TTB-I) system was lacking until our work. In the past, superconductivity in TTB-I bronzes was reported for Na_xWO_3 $0.2 < x < 0.5$, K_xWO_3 $0.4 < x < 0.57$ and $\text{Ba}_{0.13}\text{WO}_3$, but contradicting this, TTB-I $\text{K}_{0.58}\text{WO}_3$ has also been reported as a semiconductor. In the past year we completed a detailed study on the superconducting K_xWO_3 tetragonal tungsten bronze TTB-I phase. This was possible because we realized that such systems can be extremely sensitive to air and moisture exposure and thus we were able to make this study through very careful handling of the samples. Our experimental characterization was supplemented by electronic structure calculations. The calculations indicated that close to the HTB-TTB structural phase boundary, the Fermi Level in the TTB-I phase transitions through a van Hove singularity; the highest T_c in the tetragonal-I system corresponds to this doping level. This result falls in line with our other studies that have shown the maximization of superconductivity at a structural phase boundary. Finally, we presented a phase diagram for superconductivity across the full HTB, TTB-I, and CTB tungsten bronze family, which has not been previously possible. We found that the highest superconducting T_c is observed in general at the lowest electron doping level for the WO_3 framework globally (for all members of the family), and also at the lowest doping level for the HTB and TTB-I superconductors individually; it is almost independent of doping for the CTB. The new data that we have provided suggests that a modern theoretical treatment of all the compounds in this family of superconductors would be of interest.

Functionalization of Metal-Organic Frameworks - From Hydrogenase Biomimetics to Polymer Hybrids

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Funding: \$720,000 (2014-2017)

PROGRAM SCOPE

This continuing proposal in the area of Materials Chemistry describes the use of advanced synthetic methods to prepare functional metal-organic frameworks (MOFs). Many of the advanced synthetic methods that will be used to prepare functional MOFs were developed during the last funding period and have been widely adapted in the chemical community. This research program has also served to train a large number of graduate students and postdoctoral fellows, including several women and members of underrepresented groups. This continuing research program will develop new MOFs for both the production and storage of H_2 (Specific Aims 1-3). These efforts will focus on several innovative studies, all of which involve new chemistry and new materials. For H_2 production, the inclusion of functional, biomimetic hydrogenase models into MOFs will be developed (Specific Aim 1). Preliminary results show that these H_2 -producing catalysts are greatly stabilized within the matrix of a MOF. For H_2 storage, our efforts will focus on examining the MOFs containing metal-catecholato sites that have been theoretically predicted to meet 2017 DOE goals for deliverable H_2 capacity (Specific Aim 2), as well as fundamental studies on MOFs with self-organized aryl substituents that show enhancements in capacity and gating (i.e. hysteresis, Specific Aim 3). Finally, an additional topic of investigation will be on polymer-

MOF hybrid materials with emergent properties (Specific Aim 4). MOFs are being increasingly explored as templates for soft materials with a high degree of organization. Here we propose the use of 'polymeric ligands' that upon exposure to metal ions will form MOF or MOF-like porous domains. This concept is based on substantial preliminary results with crosslinked and oligomeric ligands that we have shown readily form MOFs. We will also explore these new ligands as a strategy to introduce a new class of coordinatively unsaturated metal centers into MOFs.

FY 2014 HIGHLIGHTS

Our work on the modification and functionalization of metal-organic frameworks (MOFs) in order to tune gas sorption and other physical properties of these materials has been very productive. On average, we have published more than one DOE-supported paper every-other month since the beginning of this grant. These publications have appeared in top-tier chemistry journals and many have been highlighted as 'hot articles' or 'top downloaded' articles by various journals. Some of our accomplishments include: Chem. Commun. 2013, 49, 3200-3202. The synthesis of canonical isoreticular metal-organic frameworks (IRMOFs) containing interligand crosslinks was reported. Chemically crosslinking two molecules of 2-amino-1,4-benzene dicarboxylic acid gave ligands that readily form IRMOF-1 analogs, producing crosslinked MOFs that may be designed to have novel properties. Inorg. Chem. 2014, 53, 7014-7019. A series of geometrically constrained, cross-linked benzene dicarboxylic acid (bdc) derivatives were synthesized and incorporated into the canonical isoreticular metal-organic framework (IRMOF) lattice. This work provided a new dimension to rational ligand design for metal-organic frameworks. Chem. Commun. 2014, 50, 12154-12157. The use of presynthetic and postsynthetic modification (PSM) approaches to regulate the structural organization of functional groups in the pores of isoreticular metal-organic frameworks (IRMOFs) was presented. It was found that the structural ordering of aryl groups within the IRMOF pores results in hysteretic hydrogen sorption, while the same aryl groups introduced in a disordered manner displays reversible hydrogen sorption that is more typical of the IRMOF family. Chem. Commun. 2014, 50, 5737-5740. 1,3,5-Tris(4-phosphonophenyl)benzene was synthesized via a microwave heating assisted route and used for the preparation of a new zirconium phosphonate with honeycomb-like structure displaying remarkable thermal stability and hydrolysis resistance.

EARLY CAREER: Electronic and Ionic Conductors from Ordered Microporous Materials

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Funding: \$150,000 (2014)

PROGRAM SCOPE

The proposed work aimed to establish metal-organic frameworks and covalent organic frameworks (MOFs and COFs) as new classes of high-surface area microporous electronic and ionic conductors. MOFs and COFs are crystalline materials with pore sizes ranging from 0.2 to ~ 2 nm (or larger for the latter) defined by inorganic or organic building blocks connected by rigid organic linkers. Myriad applications have been found or proposed for these materials, yet those that require electron transport or conductivity in combination with permanent porosity still lag behind because the vast majority of

known frameworks are electrical insulators. Prior to our proposal and subsequent work, there were virtually no studies exploring the possibility of electronic delocalization in these materials. Therefore, our primary goal was to understand and control, at a fundamental level, the electron and ion transport properties of this class of materials, with no specific application proposed, although myriad applications could be envisioned for high surface area conductors. Our goals directly addressed one of the DOE-identified Grand Challenges for Basic Energy Sciences: designing perfect atom and energy-efficient syntheses of revolutionary new forms of matter with tailored properties. Indeed, the proposed work is entirely synthetic in nature; owing to the molecular nature of the building blocks in MOFs and COFs, there is the possibility of unprecedented control over the structure and properties of solid crystalline matter. The goals also tangentially addressed the Grand Challenge of controlling materials processes at the level of electrons: the scope of our program is to create new materials where charges (electrons and/or ions) move according to predefined pathways.

FY 2014 HIGHLIGHTS

We have crystallized our approach towards conductive MOFs in three different formalisms: charge hopping (Marcusian transport), through-space conduction (π -stacking), and through-bond conduction (as in molecular wires). We have shown that charge hopping is responsible for charge transport in thick films of a MOF that is also electrochromic. In this context, we reported a zinc-naphthalenediimide MOF as the first material in this class that is electrochromic. This material exhibits fast switching under 60s and good coloration efficiency rivaling that of organic electrochromic polymers. In MOFs containing tetrathiafulvalene (TTF) infinite stacks, we showed that increasing the ionic radius of the constituent metal ion has the effect of pinching the inter-TTF distance, thereby causing an increase in electrical conductivity by almost three orders of magnitude. We have also demonstrated for the first time in this field metal-mediated ligand redox 'non-innocence'. Oxidation of Mn-MOF-74 (a material made from Mn^{2+} ions and 2,5-dioxidoterephthalate, DOBDC) with a Cl_2 analog (PhICl_2), resulted in transient oxidation of the Mn centers, followed by electron transfer to DOBDC. This was the first demonstration of ligand redox non-innocence in such a material, showing that the broad synthetic toolbox of molecular inorganic chemistry can be applied successfully to MOFs. Finally, by also using redox-active ligands such as hexaaminotriphenylene, we have synthesized a new material based on Ni and the imine form of the above ligand. The new material is permanently porous, and is the most conductive MOF made thus far, with a film van der Pauw (4 point probe) conductivity of 40 S/cm. This is in the same range as that of graphite and surpasses other materials in this class by nearly two orders of magnitude.

EARLY CAREER: Rational Design and Nanoscale Integration of Multi-Heterostructures as Highly Efficient Photocatalysts

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Funding: \$150,000 (2014)

PROGRAM SCOPE

The central goal of this project is to rationally design and synthesize highly complex multi-hetero-nanostructures and fundamental investigation of their potential as efficient and robust photocatalysts.

Specifically, the research program aims to integrate a nanoscale semiconductor as the light harvesting antenna with two distinct redox nanocatalysts in a single multi-hetero-nanostructure, in which the photoexcitation of the semiconductor creates electron-hole pairs that are quickly separated and transported towards the integrated nanocatalysts to drive thermodynamically uphill reactions and convert solar energy into chemical energy on site. Systematic studies have been proposed to develop general strategies for the synthesis of integrated nanostructures, and to investigate their fundamental electronic, optical and photocatalytic properties. The specific scopes include: the design and synthesis of highly complex nanostructured semiconductors for efficient harvest of solar energy through a precise control of chemical composition, physical size and the multi-heterostructure interface; the investigation of their fundamental electronic, optoelectronic properties, and optimization of the material interface for efficient charge separation, transport and photon-to-electron conversion; the development of rational chemistry to integrate the semiconductor with effective redox nanocatalysts to facilitate the interface charge transfer in photocatalytic reactions; and the investigation of such multi-hetero-nanostructures as highly efficient photocatalysts in model photocatalytic reactions.

FY 2014 HIGHLIGHTS

In the past year, we have designed and synthesized a hybrid photocatalyst by enwrapping silicon nanowires (SiNWs) with reduced graphene oxide (rGO) nanosheets to achieve greatly enhanced photoactivity and superior photoelectrochemical stability. In this novel heterostructure, the SiNWs function as the light harvest antenna; the rGO can not only function as a physical protection layer to isolate the SiNWs from the harsh electrochemical environment for greatly improved photostability, but also as a charge mediator to facilitate the charge separation and transport processes, and as the redox catalysts to ensure efficient utilization of photo-carriers for the desired redox reactions. Additionally, by using an implantation approach to dope TiO₂ nanowires with nitrogen, we have achieved a significant enhancement of visible light photoactivity in TiO₂. We have conducted systematic investigations to demonstrate that the substitutional nitrogen plays an essential role in modifying the electronic structure, optical properties and photoelectrochemical behavior of TiO₂.

Molecular Magnets Based on a Modular Approach: Investigation of Coupling, Anisotropy and Electronic Factors on Bistability

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PROGRAM SCOPE

This project is aimed at exploring the role of magnetic anisotropy in determining the properties of molecular magnets. In addition to continuing to probe the role of strong first-order spin-orbit coupling and anisotropic exchange interactions on the magnetic properties of paramagnetic molecules and assemblies that contain cyanide or reduced organocyanide bridging ligands, we are preparing new lanthanide and transition metal mononuclear Single Molecule Magnets (SMMs). The modular approach to designing homologous series of compounds has led to families of structurally related molecules with the same geometrical arrangement of spin centers; this approach continues to be exploited. Armed with

the successful elaboration of record magnetic coupling and blocking temperatures for cyanide-based SMMs, we are poised to further advance fundamental knowledge about how single-ion anisotropy profoundly manifests itself in terms of magnetic bistability. We continue to be interested in early transition metal ions from groups V and VI that have been very little explored or entirely unexplored in cyanide chemistry. We are also targeting families of mononuclear compounds of transition metal and lanthanide ions that display bistability in spite of the few number of spins that they possess, a topic that is growing quite rapidly in the literature. The concept of using organocyanide radicals as bridges for SMMs was not elaborated to any great extent in the previous grant period due to an emphasis on cyanide chemistry, but these studies are figuring prominently into this phase of the research.

FY 2014 HIGHLIGHTS

In the period since September 2014, we have made considerable progress towards the goals of the project and have submitted or have five papers published or in press. The highlights of our recent 2014 activities are as follows: Discovery of a tape-like chain based on the anisotropic building block hexacyanomanganate(III) which exhibits long-range magnetic ordering below 5.1 K as well as single chain magnetic behaviour at lower temperatures with an effective energy barrier of 40.5(7) K. An unusual feature of the magnetism is that single chain magnetic behavior in competition with long range ordering which is rare. Efforts to minimize the interchain interactions and extend this chain architecture to other cyanide building blocks are underway. The elucidation of a mononuclear trigonal bipyramidal Co(II) complex with easy-plane anisotropy that displays Single Molecule Magnet Behavior. A comparison with other previously reported Co(II) complexes with TBP coordination environments revealed that relatively minor structural changes can lead to distinct differences in the magnetic properties. Theoretical calculations to aid in determining what factors may be responsible for these differences are currently underway. Another major finding is a new erbium SMM that exhibits slow relaxation of the magnetization under zero dc field with $\Delta E_{\text{eff}}/k_B = 66.4$ K and magnetic hysteresis up to 3 K. This work helps in the refinement of the theory that oblate or prolate lanthanides must be stabilized with the appropriate ligand framework to maximize axial anisotropy in order for SMM behavior to be favored. A spin-crossover Co(II) cation in conjunction with partially charged organocyanide radicals led to the observation of a spin-transition-induced anomaly in the semiconducting behavior of a salt of Co-tris(terpy). The synergistic interactions between the semiconducting organic radical stacks and SCO properties are a consequence of structural variations with temperature.

Small Gas Storage and Selective Carbon Dioxide Capture by Nanoporous Organic Polymers

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Funding: \$200,000 (2014)

PROGRAM SCOPE

Our research targets the synthesis of porous organic polymers (POPs) that have adjustable pore size, surface area, and chemical composition for use in gas separation and storage applications. Of particular interest to our research goals is the use of N-rich POPs in selective carbon dioxide (CO₂) capture from gas mixtures such as flue, natural, and landfill gases because of the greenhouse nature of CO₂. CO₂

Capture and sequestration (CCS) from fossil fuels burning is essential for stabilizing CO₂ concentration in the atmosphere until affordable and efficient carbon-free energy sources become widely accessible. The current technology for CCS employs aqueous amine solutions to chemically trap CO₂ in the form of carbamate. In spite of its effectiveness, such adsorbents suffer many drawbacks including solvent decomposition and evaporation, toxicity, and corrosiveness in addition to the large energy penalty needed for solvent regeneration. Among the promising materials for CO₂ capture from flue gas and methane-rich gases are nitrogen-functionalized porous materials such as organic polymers, organic-inorganic hybrid materials, and porous carbons. Integrating nitrogen Lewis basic sites into the frameworks of porous organic polymers is essential for attaining high CO₂ uptake and selectivity over other gases present in gas mixtures. Several synthetic routes for N-functionalized organic polymers were evaluated wherein the basicity of the N-sites can be modified. Both pre-synthesis and post-synthesis modification methods of porous organic polymers endow polymers with enhanced CO₂ uptake and selective capture properties. Upon polymers synthesis and characterization, their performance in gas separation and storage can be evaluated using gas sorption measurements. The structure-function relationship of the polymers can be further assessed using first-principles theory, which can predict gas interaction sites and binding affinities.

FY 2014 HIGHLIGHTS

We have demonstrated the use of pyrene- and triazine-based benzimidazole-linked polymers (BILPs) in CO₂ removal from flue and methane-rich gases. The implication of different physical properties (pore size and surface area) on selective CO₂ uptake or separation from N₂ and CH₄ under pressure swing adsorption (PSA) and vacuum swing adsorption (VSA) were investigated. The Ideal Adsorbed Solutions Theory (IAST) data show that BILPs exhibit high CO₂/N₂ selectivity values. Furthermore, the optimal porosity and CO₂ enthalpy of adsorption render highly porous BILPs very efficient in landfill and natural gas separation by PSA. On the other hand, polymers that have moderate porosities and higher CO₂ binding affinities are better fit for flue gas separation by VSA. Interestingly, the diverse physical properties of BILPs and their N-rich pores place them among the top performing materials for landfill gas and flue gas separation by VSA and PSA. We used a synergistic experimental and theoretical study (DFT) to highlight the impact of material design at the molecular and electronic levels on the binding affinity and interaction sites of CO₂ with BILPs. DFT calculations indicate that CO₂ is stabilized by benzimidazole units through Lewis acid-base (N...CO₂) and aryl C-H...O=C=O interactions. We also reported the synthesis of azo-linked polymers (ALPs) that have high surface area and high CO₂ uptake at room temperature. Azo-linkage formation (-N=N-) was catalyzed by Cu(I) to link triptycene and other 3D organic building units to construct highly porous organic polymers having high N-functionality. In addition to their high CO₂ uptake, ALPs display very good selectivity toward CO₂ over CH₄ and N₂. However, their selectivity levels remain below those of BILPs. Our study indicated that the use of azo-linkage in porous organic polymers could provide physicochemically stable materials for gas separation applications.

Pore Space Engineering and Functionalization in Porous Metal-Organic Framework Materials

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Funding: \$185,000 (2013-2014)

PROGRAM SCOPE

The proposed research seeks to develop innovative and transformative synthetic concepts and methods for creating crystalline porous metal-organic framework (MOF) materials. The aim is to integrate novel architectural and chemical features for high-performance gas-sorption-based and other energy related applications. The project combines synthesis with structural and topological analysis to design materials with advanced properties. Different properties are evaluated to establish composition-structure-property correlation that can be further utilized to refine the materials design strategy. A key innovative feature of this project is its novel architectural design strategy. To efficiently harness the pore space, the project seeks to develop a new architectural design strategy called pore space engineering and partitioning, for example, through nested cage-within-cage architecture to partition the pore space into multiple smaller functionalized and size-optimized domains. This design strategy has the advantage of creating suitable pore sizes commensurate with the size of gas molecules to enhance solid-gas interactions. A versatile synthetic strategy is to use the mixed-ligand system in which properties of two ligands are complementary with one type of ligand serving as the framework-forming ligand and the other type of ligand serving as pore-space-partitioning ligand. A related strategy is to use the mixed-metal system in which two different metal types play roles of the framework formation and pore-space-partitioning separately. These two strategies can be combined to allow exquisite control over the architectural and chemical features. Such materials hold great promise for applications requiring high-capacity gas uptake, especially at or near ambient conditions.

FY 2014 HIGHLIGHTS

Prior to this study, MOFs with the highest CO₂ uptake capacity were those equipped with open metal sites. During this funding period, alternative strategies and mechanisms have been successfully developed for creating high-performance CO₂ adsorbents. Through a ligand insertion pore space partition strategy, crystalline porous materials (CPMs) with superior CO₂ uptake capacity have been synthesized. Specifically, a new material, CPM-33-Ni without any open metal sites, has been designed and it has the exceptional CO₂ uptake capacity comparable to the best performing MOF-74 with the same metal at 298 K and 1 bar. The use of MOFs for other energy-related applications was also explored. One useful property found in this funding period is the use of pre-designed MOFs for creating non-precious-metal oxygen reduction catalysts (ORR) with the potential to replace high-cost Pt-based catalysts in fuel-cell technologies. By pyrolysis of such MOFs with uniquely distributed metal sites, nitrogen-doped carbons embedded with different metallic (for example, cobalt) nanoparticles were obtained. The synthesized materials showed high electrocatalytic activity comparable to the commercial Pt/C catalyst, but with better durability and methanol-tolerance performance in alkaline conditions. In addition, a general method capable of converting neutral frameworks into cationic ones with concurrent generation of mobile anions has been developed. This method is based on differential affinity between different metal ions and anions attached to the framework metal sites. Specifically, Al³⁺ was used to strip F⁻ anions away from framework Cr³⁺ sites, leading to cationic frameworks with mobile Cl⁻ anions. The subsequent anion exchange with OH⁻ led to a porous network with mobile OH⁻ anions. New materials prepared by anion stripping showed much improved ionic conductivity. This new materials design method represents a novel approach for developing solid electrolytes for energy applications.

EARLY CAREER: Atomically Defined Edge-Doping of Graphene Nanoribbons for Mesoscale Electronics

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PROGRAM SCOPE

The outstanding transformative potential of graphene, an infinite two-dimensional sheet of carbon atoms tightly packed into a honeycomb lattice, has been recognized mostly due to its exceptionally high charge carrier mobility, thermal conductivity, and tensile strength. These undeniably very desirable properties, however, represent only a very small facet of the true potential of all- sp^2 carbon materials and its promise to revolutionize the field of molecular electronics. Graphene's most unusual characteristics can be observed when the infinite two dimensional sheet is scaled down to nanometer dimensions. The central objective of this research is to develop the technology and the tools required to synthesize and to fine-tune the properties of atomically defined graphene nanoribbons (GNR) with a particular focus on controlling the absolute dimensions (length, width), the symmetry, and the edge-substitution pattern of mesoscale carbon materials. Specific goals of this project are: To develop a complementary set of bottom-up strategies toward atomically defined GNRs from small molecule building blocks, to tune the intrinsic band gap of semiconducting GNRs by controlled edge-doping, to devise a strategy to fabricate segmented GNRs featuring heterojunction architectures, and to identify mesoscale structure-performance relationships.

FY 2014 HIGHLIGHTS

We have developed three new families of molecular building blocks for the fabrication of atomically defined GNRs from small molecule precursors on solid supports and in solution. We expanded the substrate scope for a surface catalyzed bottom-up synthesis of semiconducting armchair GNRs (AGNRs) on Au(111) surfaces. Chemical modification of a common building block gives access to 7-, 13- and 17- armchair GNRs featuring atomically smooth edge-structures varying in width between 0.7 and 2.0 nm. UHV STM imaging confirms the predicted molecular structure while dI/dV spectroscopy gives direct access to the band gap of the resulting GNRs. We have been able to perform the simultaneous copolymerization of two distinctive molecular building blocks on surfaces. The co-deposition of a precursor for 7-AGNRs and 13-AGNRs yields structures featuring a random alternating pattern of wide and narrow GNR segments. The interphase between 7-AGNRs and 13-AGNRs represents the first demonstration of the rational synthesis of a functional Type I heterojunction within an individual graphene nanoribbon. Current efforts are dedicated to explore the performance of these heterojunction devices in tunneling transistor architectures. Furthermore we explored polymer-based strategies to control the assembly of block copolymers as precursors for segmented GNRs. Living ring-opening metathesis provides access to linear poly(phenylene ethynylene) that can be converted into a polyphenylene precursor for armchair graphene nanoribbons using post polymerization benzannulation techniques. This polymeric precursor can be oxidized either in solution or on a substrate to yield the extended GNR. The inherent advantage of this technique is that the living polymerization enables the absolute control over the length and the segmentation of the GNR.

EARLY CAREER: Chemical Frustration: A Design Principle for the Discovery of New Complex Alloy and Intermetallic Phases

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PROGRAM SCOPE

Intermetallic phases represent a broad class of solid state compounds with an immense structural diversity. A limiting factor in developing materials based on the valuable physical properties exhibited by intermetallics (which can include superconductivity, thermoelectric effects, and a range of magnetic phenomena) is the difficulty of predicting or controlling their crystal structures. An emerging theme that provides an avenue toward such control is a link between structural complexity and the coexistence of competing bonding or packing types, a conflict we refer to as chemical frustration. In this project, we aim to develop the concept of chemical frustration into a predictive framework for the discovery of new complex intermetallic phases and guiding aspects of the structures of these phases. To achieve this goal, we are pursuing three main research objectives: (1) the synthesis and characterization of new complex intermetallics in systems designed to exhibit chemical frustration, (2) the creation of theoretical tools for analyzing chemically frustrated phases, and (3) the merging of our experimental and theoretical insights into guidelines for the synthesis of new phases. In our synthetic work, our strategy to induce frustration is to create ternary combinations of metallic elements such that incompatibilities arise between the preferred bonding modes of the binary subsystems. Ternary phases forming in these systems must then reconcile these conflicts, with microscopic phase segregation being one likely result. Our theoretical work is focused on developing tools for analyzing how spatial segregation in electronic features accompanies chemical frustration. One approach here is the fitting of Hückel models to DFT results and the analysis of these models with the Method of Moments, a technique which provides a direct link between local geometrical features and aspects of the electronic density of states.

FY 2014 HIGHLIGHTS

One hallmark of chemical frustration in intermetallics is the spatial segregation of differing interaction types within a crystal structure. Here we highlight two instances of this segregation that we studied during FY 2014. In our theoretical investigations of complex structures appearing on the Sc-rich side of the Sc-Ir phase diagram, we found that the stability of the phases could be understood in terms of our recently developed μ_3 acidity model. Sc metal is a strong μ_3 acid, while Ir is a moderate μ_3 base. For Sc-rich compositions, then, the majority Sc atoms are faced with the challenge of achieving neutralization with only a relatively small number of Ir atoms. The solution to this issue is found in dividing the structure into domains of two different packing types: tetrahedral close packed (TCP), where the average interaction strength is relatively strong, and simple close packed (SCP), where the average interaction strength is weaker. The Sc atoms create icosahedra around the Ir atoms, forming TCP units to maximize Sc-Ir interactions. The Sc-Sc contacts outside of these icosahedra are arranged to create octahedra, units found in SCP arrangements, so that the interference of Sc-Sc interactions in the neutralization process is reduced. Our second example is the structure of Ta_4Ga_5 , a phase we synthesized that exhibits a new binary structure type. While in binary phases, heteroatomic interactions

are generally considered to provide the dominant impetus for phase formation, in this phase substantial homoatomic clustering is observed in both the Ta and Ga sublattices. Our electronic structure analysis revealed that this clustering emerges from the drive of the Ta atoms to achieve 18 electron configurations with only a small number of electrons. Ta-Ta clustering allows covalent sharing of electrons, with the Ga atoms then being positioned to the outskirts of the clusters to preferentially stabilize Ta-Ta bonding functions over antibonding ones.

Towards Molecular Engineering of Polymer Glasses

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Funding: \$175,000 (2014)

PROGRAM SCOPE

Glass-formation has been central to fabrication technologies since the dawn of civilization. An understanding of polymer glass-formation is essential to design advanced glassy materials with applications in high resolution photoresists, electronics, non-linear optics, nano-imprint patterning (for memory storage and device fabrication), organic photovoltaics and plastic crystals (for batteries), polymer films (as coatings and templates), and in energy storage, generation and power conversion where polymeric glasses are structural entities. The huge variations of 14 orders of magnitude in the viscosity, structural relaxation time and other dynamical properties over rather narrow temperature ranges are universal properties of glass-formation are common to both small molecule and polymeric glass-formers and impede theoretical progress. Despite the fundamental nature of glass-formation and the regularities observed in this process, a generally accepted theoretical description of this ubiquitous and conceptually vexing form of matter remains elusive. The present project seeks to rectify this deficiency by extending and applying our theory that explains the universal characteristics of glass-formation and the dependence of the physical properties of polymer glass-formers on molecular structure, molecular weight, pressure, temperature, etc. The focus of the present project is to extend our generalized entropy theory of glass formation a) to describe the combined influence of chain stiffness and cohesive energy on the glass transition temperature and the fragility, the two quantities that determine whether the material can be processed by extrusion, casting, ink jet, etc., b) to extend this treatment to describe the influence of polar side groups on the properties of polymer glass-formers, and c) to extend the theory to treat polymer melts and explain the molecular factors governing the appearance of two structural relaxation times in partially miscible polymer blends.

FY 2014 HIGHLIGHTS

Despite the long-recognized fact that chemical structure and specific interactions greatly influence the thermodynamic properties of polymer systems, a predictive molecular theory that enables systematically addressing the role of chemical structure and specific interactions has been slow to develop even for polymer melts. Our analysis of the combined impact of the microscopic cohesive energy and chain stiffness on the magnitudes of the fragility parameter and the glass transition temperature of polymer glass-formers predict that polymers with rigid structures and weak nearest neighbor interactions are the most fragile, while the glass transition temperature becomes larger when

the chains are stiffer and/or nearest neighbor interactions are stronger. The work leads to the identification of some important design concepts, such as iso-fragility lines where several thermodynamic properties are found to remain invariant. We have introduced a major extension of our theory to describe the dependence of the fragility and glass transition temperature of polymer melts upon the presence of polar groups in the chain side groups in order to provide guidance for the control of glass properties by modification of the polar groups. Computations based on this theory are currently in progress. Most technological polymer materials are mixtures, called blends, of different polymers chosen to achieve desired properties. Thus, we have begun the extension of our generalized entropy theory to describing the perplexing appearance of two structural relaxation times in the one phase region of partially miscible blends where a single relaxation time is expected. The theory successfully explains this phenomenon and why the relaxation of the one phase system behaves like a composite material.

Cathode Catalysis in Hydrogen/Oxygen Fuel Cells: New Catalysts, Mechanism, and Characterization

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Funding: \$350,000 (2014)

PROGRAM SCOPE

In this project, we are engaged in a comprehensive plan of research directed at developing new catalysts and new understandings relevant to the operation of low temperature hydrogen-oxygen fuel cells. The focal point of this work is one centered on the Oxygen Reduction Reaction (ORR), the electrochemical process that most fundamentally limits the technological utility of these environmentally benign energy conversion devices. It is therefore to the single greatest challenge limiting wide-spread implementation of hydrogen-oxygen fuel cells -- providing robust low cost cathodes that efficiently reduce dioxygen to water -- that we address the work described in this project. Utilizing support from this project, we developed a new class of ORR catalysts, based on Cu dimers and multimers. These new materials exhibit ORR onsets at potentials higher than any other Cu-based material in neutral and basic environments and are inspired by the three-Cu active site in laccase which has the highest ORR onset potential of any material known. Over the last grant period, we synthesized a series of Cu trimers, and interrogated their activity. Based on these results, we will focus our efforts going forward on further synthetic and characterization of different Cu trimers. A feature of the program will evaluate the stability of these supported catalysts and develop methods to enhance catalyst survival on the electrode. Insight from characterization activities will inform synthetic efforts.

FY 2014 HIGHLIGHTS

In 2014 we showed that we could measure the stress-thickness of a Pt surface with and without the presence of O₂. In the presence of O₂, the stress-thickness curve is displaced in a more compressive direction over the entire potential window interrogated, which shows that the Pt surface dynamically responds to the presence of O₂ by Pt-Pt bond elongation. Interestingly, the stress calculated from EXAFS-

derived Pt-Pt bond length changes match very well with those from the corroborating surface stress measurements. This is a new method to examine strains arising from electrochemical reactivity as a consequence of adsorbate association with the electrode. We also designed a robust, active, dinuclear Cu oxygen reduction reaction (ORR) catalyst embedded inside a hybrid bilayer membrane (HBM) system. We demonstrated that proton delivery to the catalyst through the lipid layer can be controlled through the use of an alkyl phosphate proton carrier. Specifically, we showed that we could use the HBM to switch the ORR on and off, a so-called 'pcet switch', by changing the ability of the proton delivery agent to transport protons through the lipid layer. We further used the HBM as an electrochemical platform to study anion diffusion through a lipid monolayer. Our results demonstrate that anion transport in a HBM is best described by the solubility-diffusion mechanism, not the pore mechanism. We envision this approach can be used ultimately to acquire unique mechanistic insight into PCET reactions, including the rate of O–O bond cleavage of the bound oxygen species. We also examined the temperature dependence of the ORR in a high pressure, high temperature reactor, showing that (as expected) increasing the temperature leads to increased ORR rates.

Low-Temp Synthesis of Carbide-Derived Carbons from Binary and Ternary Carbides in the Si-Ti-C Systems

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Funding: \$240,000 (2013-2014)

PROGRAM SCOPE

Carbide-derived-carbons (CDCs) are a growing class of nanostructured carbon materials with properties that are desirable for many applications. The scope of the current project is to gain a fundamental understanding of CDC formation at room temperature through electrochemical etching. The major research tasks were: 1. Room-temperature electrochemical etching of binary (e.g. SiC and TiC) and ternary carbides (e.g. Ti₃AlC₂ and Ti₃SiC₂ MAX phases) to produce CDCs; 2. Parameter study of CDC formation conditions, such as different etching electrolytes, electrochemical conditions, types of the starting carbides, etc.; 3. Characterization of structure and properties of CDCs produced by electrochemical etching; 4. Characterization of electrochemical properties of the as-produced materials. The current project was expected to produce new carbon materials with unique structures, pore networks and surface chemistry using an energy efficient method. Furthermore, we also expected to explore the possibility of selective etching of metal atoms from ternary carbides for synthesis of novel two dimensional carbide structures.

FY 2014 HIGHLIGHTS

A summary of the accomplishments is listed as follows: (1) Room-temperature synthesis of CDC film from binary carbide SiC [1]: The selective extraction of Si from SiC was achieved by electrochemical etching with hydrofluoric acid (HF) in different organic solvents. The role of polarity, surface tension, density, and viscosity of the organic solvents was investigated. Formation of ordered carbon on the surface of etched SiC was confirmed. (2) Room-temperature synthesis of CDCs from ternary carbide - the MAX phases [2]: We succeeded in selective extraction of metal atoms from the ternary layered carbides, Ti₃AlC₂, Ti₂AlC and Ti₃SiC₂ (MAX phases) at ambient temperature. The result is a predominantly

amorphous CDC with a narrow distribution of micropores around 0.5 nm. This process can be achieved by placing the carbides in HF, HCl or NaCl solutions and applying anodic potentials. The etching kinetics for Ti_3AlC_2 in HF was quantified. (3) Room-temperature synthesis of carbon/sulfur nanolaminates from the MAX phase Ti_2SC [3]: We achieved, for the first time, the selective extraction of the M element (Ti) from the Ti_2SC MAX phase to form carbon/sulfur, C/S, nanolaminates at room temperature by electrochemical etching. Covalent bonding between C and S is observed, which renders these nanolaminates promising candidates as electrode materials for Li-S batteries. It is also possible to extract Ti from other MAX phases, such as Ti_3AlC_2 , Ti_3SnC_2 , and Ti_2GeC , suggesting that electrochemical etching is a general method for selectively extraction of the 'M' elements from the MAX phases, to produce a new family of materials - 'AX' layered structures. The latter in turn hold promise for a variety of applications, such as energy storage, catalysis, etc. References: [1] Senthilnathana J, *et al.* Synthesis of Carbon Films by Electrochemical Etching of SiC with Hydrofluoric Acid in Nonaqueous Solvents, *Carbon*, 2014, 71, 181-189. [2] M. R. Lukatskaya, J. Halim, B. Dyatkin, M. Naguib, Y. S. Buranova, M. W. Barsoum, Y. Gogotsi, Room-temperature carbide derived carbon synthesis by electrochemical etching of MAX phases, *Angewandte Chemie Int. Edition*, 2014, 53 (19) 4877-4880 (cover article). [3] M.-Q. Zhao, M. Sedran, Z. Ling, M.R. Lukatskaya, O. Mashtalir, M. Ghidui, B. Dyatkin, D. J. Tallman, T. Djenizian, M. W. Barsoum, Y. Gogotsi, Synthesis of Carbon/Sulfur Nanolaminates by Electrochemical Extraction of Titanium from Ti_2SC , *Angewandte Chemie, Int. Edition*, 2015, DOI: 10.1002/anie.201500110R1 (VIP article).

Materials and Interfacial Chemistry for Next-Generation Electrical Energy Storage

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Funding: \$700,000 (2014)

The Oak Ridge National Laboratory part of this project is listed separately under Principal Investigator: Sheng Dai.

PROGRAM SCOPE

Electrochemical energy storage systems are critically needed for electric vehicles and for effective use of renewable energy sources. Cost, cycle life, safety, energy, and power density are all parameters that depend critically not only on the materials used and their morphologies for the different battery components, but also on their compatibility with one another and, therefore, on the chemistries at their interfaces. Factors influencing cost include the materials and fabrication costs, cycle and calendar life, and the management requirements for safety and life of a battery consisting of many cells. The present-day battery technologies fall short of the requirements for electric vehicles and stationary grid storage. Alternative strategies must consider ways to increase safely the voltage and capacity of the individual cell without compromising rates of working-ion transfer between the anode and the cathode. Can new strategies allow the use of metallic Li or Na anodes and liquid flow-through or air cathodes in place of insertion compound hosts? If not, can alloy anodes be tailored to permit a fast charge at minimum cost in cell voltage and in irreversible capacity loss on first charge? Can multiple-electron redox couples be used? This project addresses several of such key material questions associated with both alternative battery strategies and the stretching of present strategies. The program of work involves intuitive design of new materials based on basic chemistry/physics principles, novel chemical synthesis approaches, and

advanced *ex situ* and *in situ* characterization in order to establish an understanding of how to optimize the basic structure-composition-property relationships. The basic understanding gained through the proposed program of work is critical for realizing next-generation electrical energy storage systems with long life at an affordable cost, alleviating our dependence on foreign oil and CO₂ emissions.

FY 2014 HIGHLIGHTS

The project focused on the following aspects this year: (1) new composite porous-polymer/oxide membranes as separators that block dendrites from an alkali-metal anode, (2) low-cost electrocatalysts and novel cell configurations for hybrid lithium-air batteries, (3) carbon-coated separators for lithium-sulfur batteries, (4) high-voltage cathodes for lithium-ion batteries, (5) new cathodes for sodium-ion batteries, and (6) nanocomposite alloy anodes for lithium-ion and sodium-ion batteries. We have developed low-cost porous-polymer/oxide composites saturated with the conventional organic liquid-carbonate electrolyte that act as flexible and mechanically robust separators and block anode dendrites. We have developed low-cost nitrogen- and oxygen-doped carbons for the oxygen reduction reaction and low-cost nickel cobalt oxide catalysts grown on nickel-metal foam for the oxygen evolution reaction; these catalysts in a decoupled cell configuration exhibit performance and durability superior to conventional noble-metal catalysts. We have also developed a low-temperature form of lithium cobalt oxide as a bifunctional catalyst. A thin layer of microporous carbon coated onto a polymer separator traps the dissolved polysulfides and improves significantly the cycle life of lithium-sulfur cells. We have explored doping and heat treatment to stabilize the high-voltage lithium manganese nickel oxide spinel cathode against reaction with the electrolyte. An insertion compound for the cathode of a sodium-ion battery is normally either a layered compound or has a framework structure containing a polyanion. We have investigated vanadium fluorophosphate cathodes for a sodium-ion battery. With an aim to realize fast charge with both lithium-ion and sodium-ion batteries, we have explored a number of nanocomposite alloy anodes consisting of intermetallic active components such as FeSb and an inactive component such as TiC or aluminum oxide, which exhibit life over 500 cycles.

Cyclometalation Syntheses of Phosphorescent Complexes

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Funding: \$150,000 (2013-2014)

PROGRAM SCOPE

This award in Basic Energy Sciences supports fundamental research in organometallic materials. Specific targets are organometallic complexes that act as light-emitting elements in electroluminescent devices. Transmetalation reactions from boron precursors are being developed as synthetic methods leading to cyclometalates that, by design, are phosphorescent. Reaction of ligand precursors bearing boronic acids or boronate esters with metal complexes and a supporting base leads to metal-carbon bond formation, possibly coupled to closure of a chelate ring. The new method is mild and high-yielding; redox side-reactions are avoided. Metals of immediate importance include iridium, copper, platinum, and gold. New families of complexes are sought through boron transmetalation methods, and new compounds are characterized by ground state and optical methods.

FY 2014 HIGHLIGHTS

A new synthetic method for gold-carbon bond formation that relies on arylboronic acids, a supporting base, and palladium catalysis was published. Cyclometalated gold(III) chloride complexes react as electrophiles in palladium-mediated Suzuki-Miyaura coupling reactions. Both mono- and diarylation reactions have been demonstrated. The first aryl to bind gold does so opposite nitrogen; the shorter (and presumably stronger) gold-chloride bond is sacrificed first. An arylation mechanism was proposed where oxidative addition of the Au-Cl bond to palladium is coupled to a rearrangement that yields the thermodynamically stable mono-aryl. The new complexes are triplet-state lumophores. The first fluoride-bridged cyclometalated iridium(III) dimers have been identified as high-efficiency lumophores, some with quantum yields exceeding 50%. Emission lifetimes are microsecond-length at room temperature, and emission profiles show vibronic structure indicating ligand dominance of the light-emitting state(s). One such complex has been crystallographically characterized. Static and time-dependent density-functional theory calculations indicate that phosphorescence originates from perturbed ligand-centered states.

Solid State Electronic Structure and Properties of Neutral Carbon-Based Radicals

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Students: 2 Postdoctoral Fellow(s), 1 Graduate(s), 1 Undergraduate(s)
Funding: \$242,000 (2014)

PROGRAM SCOPE

The goal of our work is the synthesis and characterization of a new class of organic molecular metals and superconductors based on neutral carbon-based spin = ½ radicals. Our current molecular family of choice is the spiro-bis(phenalenyl)boron radicals, and they remain the only class of neutral carbon-based radicals that may be crystallized and studied in the solid state without requiring bulky substituents to inhibit σ -dimerization.

FY 2014 HIGHLIGHTS

Substitutional doping is an extremely important industrial process, most notably in the semiconductor industry where crystalline silicon is doped with atoms from neighboring columns of the periodic table such as boron or nitrogen to create holes or electrons in the lattice, thereby modulating the carrier concentration and the electrical properties. Such an approach has never been successfully applied to organic molecular solids. By making use of a spiro-bis(phenalenyl)boron radical we have been able to grow substitutionally doped organic crystals directly from solution in which the carrier concentration is systematically varied by the introduction of dopant molecules into the lattice which differ only by the replacement of boron with beryllium. The method depends on the use of a host lattice composed of spiro-bis(phenalenyl)boron radicals, and by co-crystallization from solutions of spiro-bis(9-oxidophenalenone)boron radical $[\text{PLY}(\text{O},\text{O})]_2\text{B}$ mixed with select amounts of spiro-bis(9-oxidophenalenone)beryllium $[\text{PLY}(\text{O},\text{O})]_2\text{Be}$ we are able to isolate a series of solid state solutions of composition $[\text{PLY}(\text{O},\text{O})]_2\text{B}_{(1-x)}\text{Be}_x$. The dopant molecules $[\text{PLY}(\text{O},\text{O})]_2\text{Be}$ serve to introduce holes into the lattice of spins provided by the $[\text{PLY}(\text{O},\text{O})]_2\text{B}$ radicals and lead to a systematic increase in the

conductivity while decreasing the activation energy of the conduction process and leaving the solid state structure relatively unperturbed. While the energies of the hole sites are expected to be high, the results are consistent with the interpretation of the electronic structure of $[\text{PLY}(\text{O},\text{O})]_2\text{B}$ in terms of the resonating valence bond (RVB) model.

EARLY CAREER: Crystallization-Driven Assembly of Conjugated-Polymer-Based Nanostructures

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Principal Investigator: Ryan Hayward
Sr. Investigator(s):
Students: 1 Postdoctoral Fellow(s), 4 Graduate(s), 0 Undergraduate(s)
Funding: \$150,000 (2014)

PROGRAM SCOPE

This project focuses on harnessing solution-state crystallization of conjugated polymers to construct well-defined crystalline building blocks that will facilitate fabrication of optoelectronic devices, especially photovoltaic cells, in scalable and cost-effective ways. We seek to provide transformative impacts on the control of organization, and therefore the electronic properties, of matter on three different length-scales: 1) the molecular scale, in the sense of achieving highly crystalline semiconducting polymer-based materials capable of efficient charge transport, 2) the nanoscale, in terms of positioning n- and p-type materials with domain sizes comparable to exciton diffusion lengths (~ 10 nm) to facilitate charge separation, and 3) the colloidal scale, such that well-defined crystalline nanoscale building blocks can be hierarchically organized into device layers with optimal structures. The project relates to the mission of the DOE Basic Energy Sciences program, which seeks to “...understand, predict, and ultimately control matter and energy at the electronic, atomic, and molecular levels...”² and the Materials Chemistry program’s goals of supporting “new chemical means to direct and control the non-covalent assembly of materials, such as strategies to organize electron donors and acceptors”² and “to control and design interfaces between dissimilar materials”.

FY 2014 HIGHLIGHTS

During FY 2014, the project has led to major advances in three areas: 1) tailored growth of acceptor nanowires using conjugated polymer additives; 2) controlled nucleation of conjugated polymer nanofibers; 3) enhanced stability and functionalization of conjugated polymer nanofibers. First, we found that polythiophenes serve as crystal modifiers during growth of perylene diimide (PDI) crystals, providing great flexibility for tailoring PDI crystal size and morphology. Adsorption of poly(3-hexyl thiophene) (P3HT) to PDI crystals slows their growth and promotes formation of high aspect-ratio nanowires. Coupled with ultrasound to facilitate crystal nucleation, this yields PDI nanowires with highly uniform lateral dimensions down to 20 – 30 nm. Short PDI nanowires can be extended, leading to well-controlled nanowire lengths and branched crystal architectures. Second, we have established that graphene surfaces can be used as highly selective nucleating agents for growth of P3HT crystals from metastable solutions. Under conditions where homogeneous nucleation of P3HT is very slow, but the equilibrium degree of crystallinity is high, nanofibers grow selectively on multilayer graphene or highly oriented pyrolytic graphite. These results provide a useful platform for further fundamental studies of crystal growth, and a possible route toward solution processed, vertically oriented semiconducting polymer nanofibers. Finally, using a copolymer of P3HT and a polythiophene bearing an azide group, we

have demonstrated robust and easily functionalized polymer nanofibers. Remarkably, the azide group is incorporated at molar ratios of up to 0.2 without disrupting the solution crystallization of the polymers, or their charge-transport properties. Subsequent photo-crosslinking renders the fibers stable against solvent and temperature treatments, while the presence of excess azides allows for 'click' functionalization, for example to yield dispersion in polar solvents including water.

Optical Spectroscopy and Scanning Tunneling Microscopy Studies of Molecular Adsorbates and Anisotropic Ultrathin Films

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Funding: \$534,000 (2014-2017)

PROGRAM SCOPE

The emphasis of our research is to develop sufficient fundamental understanding to allow the controlled preparation of nano-, and meso-structured surfaces with novel optical properties and chemical reactivity. The research places an emphasis on the synthesis of, sometimes complex, surface structures under conditions that allow for detailed control and understanding of the composition and structure and the subsequent relationship to properties and chemical reactivity. In this research we combine the use of optical probes with surface imaging experiments (electron microscopy (SEM, TEM), and variable temperature ultra high vacuum scanning tunneling microscopy (STM)). These experiments are combined with UHV surface spectroscopies (High Resolution Electron Energy Loss Vibrational Spectroscopy (HREELS), Auger electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS) and thermal desorption spectroscopy (TDS)). We use a combination of STM and SEM/TEM to study the growth of mesoscopically ordered nanometer sized metal and metal oxide structures on well defined substrates such as highly ordered pyrolytic graphite (HOPG). We will continue to develop methods (e.g. photoelectrochemical deposition) to decorate nanometer scale metal oxide structures with transition metal nanoparticles generating Nanoparticles on Nanoscale substrate materials (NpNs). The electronic structure and chemical properties of these new structures will be studied and contrasted with those of the more conventional nanoparticles on macroscopic substrate materials.

FY 2014 HIGHLIGHTS

During the 2014 fiscal year we have (1) completed a scanning tunneling microscopy study of the dehydrogenation of mono-olefins on aluminum oxide films that are decorated with Pt nanoparticles. Our experiments demonstrate that while small Pt nanoparticles on alumina are active for the dehydrogenation of mono-olefins this does not lead to carbon particle formation on the Pt nanoparticles as happens on macroscopic Pt surfaces. Rather at high temperatures spill-over from the Pt onto the alumina occurs. Carbon that spills onto the alumina does not form graphite even at high temperature, rather carbon clusters are formed at the grain boundaries of the alumina film, (2) developed methods simple methods for the preparation of a high density of iron oxide nanoparticles on highly oriented pyrolytic graphite and characterized these iron oxide nanoparticles using SEM, TEM, and synchrotron based x-ray photoelectron spectroscopy and x-ray absorption spectroscopy, (3) developed

photoelectrochemical deposition methods to deposit Pt nanoparticles on the high density of iron oxide nanoparticles, and (4) studied the catalytic activity of the Pt decorated iron oxide nanoparticles.

Relationships Between the Adhesion, Friction and Nano/Micro-Structure of Materials, Surfaces and Films

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Sr. Investigator(s):
Students: 1 Postdoctoral Fellow(s), 2 Graduate(s), 1 Undergraduate(s)
Funding: \$846,000 (2014-2017)

PROGRAM SCOPE

There are two main focus areas, I and II, which are divided into 4 sub-projects. The two focus areas are: I Continue to apply recently developed, and develop new, experimental techniques based on the Surface Forces Apparatus (SFA) to measure and characterize complex dynamic molecular interaction potentials and force-laws between various surfaces in air or liquids at the atomic (sub-nano) level to gain fundamental understandings of adhesion, friction, lubrication and wear (damage) to surfaces of 'engineering interest'. These are not ideal-atomically smooth surfaces, which are now well understood, but rough or micro- or nano-structured (patterned, textured) surfaces; and in particular investigate the dynamics, i.e., the roles of rate, time, and previous history on these highly non-equilibrium interactions. Develop equations/models for the adhesion, friction and wear for such surfaces, similar to what is currently available for smooth, homogeneous surfaces and materials. II Correlate chemistry with the measured (physical) interaction forces by further developing and applying new experimental techniques for measuring the above and other types of interactions (see below) while simultaneously measuring and controlling the voltages and currents between or flowing through the solid-liquid interfaces, including any dissolution/adsorption, to establish the (electro)chemical reactions going on at each interface. The liquid films between the two surfaces can be aqueous (water based) or non-aqueous (e.g., oils, lubricant fluids, ionic liquids). The 4 sub-projects: The two focus areas are divided into 4 distinct sub-projects: (1) Adhesion, friction and wear; (2) self-sealing/self-healing interfaces; (3) new experimental techniques for electrochemical studies using both conducting and non-conducting surfaces; and (4) physical and electrical properties of non-aqueous liquids (ionic liquids, liquid crystals) in thin films, for energy storage and imaging applications.

FY 2014 HIGHLIGHTS

(1) Adhesion, friction and wear/damage: We have measured the adhesion, friction and wear of randomly rough and patterned surfaces, both 'dry' and 'lubricated', and developed a Johnson-Kendall-Roberts (JKR)-type model in terms of effective stiffness and adhesion energy parameters that quantitatively described their 'adhesion/contact mechanics' and friction behavior. We also found that, in general, damage is not directly related to the friction coefficient but to the existence of 'stiction' and/or stick-slip', rather than smooth, sliding. These findings should enable the design of surfaces and lubricant fluids to avoid costly material damage of working surfaces. (2) Self-sealing interfaces: We have synthesized and processed a new class of polymer materials that on being cut expose multiple H-bonding groups that readily reseal on bringing the surfaces back together, even in aqueous solutions. Such materials are important for both biomedical and non-biological applications. New experimental

techniques for electrochemical studies: We further developed the electrochemical (EC-SFA) allowing direct quantitative (model-independent) simultaneous measurements of physical interaction forces and chemical reactions in liquids in real time, and have applied this to a number of phenomena, including surface dissolution, identification of reacting species, corrosion, etc. – see below. (3) Molecular properties of non-aqueous liquids in thin films using the EC-SFA: Our new results on ionic liquids show that with increasing temperature the concentration of excess ‘free’ (conducting) ions increases. This work validates a previous model and is relevant for energy storage devices such as batteries. We also measured the molecular forces while imaging electric-field induced structuring and flow of confined liquid crystal molecules, opening up new methods in liquid crystals research. Award: The PI was awarded the 2013-14 Tribology Gold Medal – “the world’s highest honor in tribology”.

EARLY CAREER: Theory and Simulations of Tailored Assembly in Rod-Coil Polymer Nanocomposites

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Sr. Investigator(s):
Students: 1 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding: \$150,000 (2014)

PROGRAM SCOPE

The focus of the proposed research is to use molecular simulations to link molecular features of conjugated polymers (electron donors) and fullerene derivatives or hybrid nanoparticles (electron acceptors) to the morphology of the polymer nanocomposite. We have developed and validated appropriately detailed coarse-grained models to capture the experimentally relevant length and time scales in our simulation. We have then made predictions that serve as design rules on how changing each molecular feature would allow one to tailor the composite morphology.

FY 2014 HIGHLIGHTS

Since October 1 2013 to September 30 2014 we have published 8 peer-reviewed papers in journals including Macromolecules, ACS Macroletters, and Soft Matter. PI Jayaraman has given 9 invited talks (including talks at AIChE, ACS and XPV meetings and department seminars) where DOE supported results were presented. Jayaraman's students also presented posters and talks at APS march meeting, AIChE annual meeting, MRS fall meeting and XPV (excitonic photovoltaic) meeting. Student Ms. Hilary Marsh won Best Research Poster award for her DOE supported work at the XPV meeting.

Fundamental Studies of Charge Transfer in Nanoscale Heterostructures of Earth-Abundant Semiconductors for Solar Energy Conversion

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Robert Hamers; Wisconsin-Madison, University of
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Funding: \$500,000 (2014)

PROGRAM SCOPE

We create new earth-abundant semiconductor nanostructures and their heterojunctions with well-defined surface chemistry and develop new laser spectroscopies and atomic force microscopy integrated with ultrafast spectroscopy that probe charge transport at the quantum mechanical level in nanoscale heterostructures. They provide the fundamental understanding required to enable transformative coherent solar energy nanotechnologies.

FY 2014 HIGHLIGHTS

We discovered that chemical exfoliation of nanostructures of MoS_2 , WS_2 , and other layered MX_2 materials and the simultaneously conversion of the MX_2 material from its semiconducting 2H to the metallic 1T polymorph result in dramatically enhanced electrocatalytic activity for hydrogen evolution reaction (HER). Structural characterization and electrochemical studies confirm that the metallic MX_2 nanosheets exhibit facile electrode kinetics, low-loss electrical transport, and possess a proliferated density of catalytic active sites, which made these metallic 1T- MX_2 nanosheets highly competitive earth-abundant HER catalysts. Furthermore, 1T- MoS_2 nanosheets have been coupled to p-type silicon to enable highly efficient solar-driven hydrogen evolution due to the excellent HER activity of 1T- MoS_2 and the high-quality catalyst-semiconductor interface. We have also developed vertical heterostructures of MX_2 materials enabled by van der Waals epitaxy. MoS_2 , WS_2 , and WSe_2 layers were grown uniformly onto microplates of SnS_2 via mild CVD growth and the heteroepitaxy was unequivocally characterized. New photoluminescence properties emerge due to electronic coupling and charge separation between MoS_2 and SnS_2 . We have further expanded the nanoscale heterostructures to QDs linked with MoS_2 nanosheets. The charge transfers across the heterostructures could be important for enabling heterojunction solar conversion devices. We have used multiresonant coherent multidimensional spectroscopy to probe the dynamics of the electronic states in MoS_2 . The coherent and incoherent dynamics of the substructure of states within the A and B excitons of MoS_2 have been revealed. The narrow anti-diagonal width represents the excitonic homogeneous width resulting from coherence dephasing and the diagonal width represents the inhomogeneous width determined by the different environments. The population dynamics that appear at longer negative delay times show how energy flows between states.

Bi-Continuous Multi-Component Nanocrystal Superlattices for Solar Energy Conversion

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Nader Engheta; Pennsylvania, University of
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Funding: \$760,000 (2014)

PROGRAM SCOPE

Our program explores three-dimensional multi-component nanocrystal (NC) superlattices, wherein combinations of NCs self-assemble into well-defined, crystalline architectures. We focus on crystal

structures having bi-continuous NC sub-lattices and identify n- and p-type semiconductor building blocks that form Type-II energy offsets to drive charge separation onto electron and hole transporting sub-lattices and provide wide coverage of the solar spectrum. We aim to discover the design rules and optimize the architectures of bi-continuous, multi-component NC superlattices to efficiently convert solar radiation into electricity. Our interdisciplinary team combines NC synthesis, assembly, and structural characterization with optical spectroscopy, electrical measurements, and modeling of nanoscale materials to uncover the physical phenomena that govern the flow of energy and the transfer and transport of charge important in converting solar energy into electricity.

FY 2014 HIGHLIGHTS

We demonstrated the deposition of ordered, polycrystalline nanocrystal (NC) superlattices over large, 4" wafer scales via dipcoating of NCs. This method extends to the assembly of several bi-continuous, binary NC superlattices including AlB_2 , NaZn_{13} , CaCu_5 and MnZn_2 structures. We combined grazing-incidence and transmission small-angle x-ray diffraction with electron microscopy studies to characterize ordered NC superlattices. X-ray mapping enabled us to statistically characterize the grain size, orientation, uniformity, strain or crystal projections and polymorphs to complement real-space imaging of the superlattices. Building on our previous work demonstrating high-mobility, extended-state transport in NC assemblies, we used optical spectroscopies and electrical measurements to probe the transition from localized to extended-state transport as we engineer NC coupling via ligand exchange and carrier type and concentration via doping. In CdSe NC assemblies, we used low-temperature ultrafast spectroscopies to show that the ligand exchange and annealing, which yields enhanced interparticle coupling, is consistent with faster surface state electron trapping. Gate-controlled, low-temperature resistance and magnetotransport measurements on indium-doped CdSe NC thin films indicates that the gate induces electron accumulation and increases the localization product (localization length times dielectric constant) describing transport. Our measurements suggest the gate bias delocalizes electrons beyond the NC diameter, consistent with a decrease in the mobility gap to an insulator-metal transition. In PbS and PbSe NC assemblies we showed that the polarity and magnitude of transport depends on the contact metallurgy, the strength of NC coupling, and the surface passivation and doping. With increased coupling and doping, we observe an insulator-metal transition and fabricate high-performance n-type and p-type transistors, from which we demonstrate complementary NC circuits.

Molecular Designed Localized Static Charging for Energy Efficiency in Organic Electronics

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Sr. Investigator(s): Daniel Reich; Johns Hopkins University
Students: 1 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding: \$275,000 (2014)

PROGRAM SCOPE

The goal of this project is to synthesize charged dielectric heterostructures and evaluate their effects on adjacent and overlying organic semiconductors. The dielectrics are predominantly polystyrenes with different capabilities to accept and stabilize implanted static charge designed therein. These polymers are synthesized by a combination of chain, controlled radical, and postfunctionalization methods. The use of these static charges to control mirror charges in organic semiconductors will increase the

efficiency of organic semiconductor devices in both transistor and diode structures and also enable improved mechanisms for energy conversions, such as from electricity to light. New organic semiconducting polymers are synthesized to be compatible with the dielectric heterostructures. The heterostructures, in both vertical and lateral geometries, are characterized by morphological methods such as atomic force microscopy, scanning Kelvin probe microscopy, x-ray reflectivity, XPS/Auger depth profiling, and neutron scattering, as well as electronic methods such as determination of transistor characteristics, capacitance-voltage, thermally stimulated discharge, and charge extraction in a linearly-increasing voltage (CELIV) method. Poisson's equation modulation of voltage profiles gives charge densities as a function of distance from semiconductor interfaces.

FY 2014 HIGHLIGHTS

Polystyrenes with strong donor or acceptor side chains, as well as controlled crosslinking functional group densities, have been synthesized. Polystyrene heterostructures with different functional groups have been made. The fidelity of heterostructure formation was characterized by x-ray reflectivity and neutron scattering, from which scattering length densities and interfacial roughnesses could be calculated. Transistors using these polystyrenes as gate insulator materials have been demonstrated, including current modulations arising from charging of the polystyrene layers. Use of the heterostructures in gate materials is in progress. Lateral organic field-effect transistors (OFETs), consisting of a polystyrene (PS) polymer gate material and a pentacene organic semiconductor (OSC), were electrically polarized from bias stress during operation or in a separate charging step, and investigated with scanning Kelvin probe microscopy (SKPM) and current-voltage determinations. The charge storage inside the polymer was indicated, without any alteration of the OFET, as a surface voltage with SKPM, and correlated to a threshold voltage (V_T) shift in the transistor operation. The SKPM method allows the gate material/OSC interface of the OFET to be visualized and the surface voltage variation between the two gate material interfaces to be mapped. The charge distribution for three samples derived from the surface voltage maps using Poisson's equation agreed with those derived from the V_T shifts and the lateral gate-OSC capacitance. This is the first demonstration that surface voltage on a working OFET gate material can be related to the quantity of static charge responsible for bias stress and nonvolatility in OFETs.

Unconventional Clathrates Based on Transition Metal Pnictides: A Paradigm-Shifting Approach to Materials with Enhanced Thermoelectric Properties

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Funding: \$150,000 (2014)

PROGRAM SCOPE

Thermoelectrics convert heat into electric energy and vice versa and as such are promising materials for waste heat reduction or recovery. The development of novel materials where charge and heat transport are partially de-coupled is a key factor for the next generation of thermoelectrics. If significant breakthroughs in the area of thermoelectrics materials are to be achieved, new classes of bulk materials need to be discovered. This project seeks to develop a new class of bulk thermoelectric materials with

record-breaking characteristics. Materials where charge and heat transport are de-coupled will be found among semiconducting Zintl clathrates with a host-guest type of structure. In the crystal structure, guest cations are encapsulated within the oversized polyhedral cages of a 3D host framework. In this project we seek new thermoelectric clathrate and clathrate-like materials with frameworks comprised of the late transition metals and pnictogens, group 15 elements, P, As, or Sb. The rattling of guest cations situated in the framework cages provide effective scattering of heat carrying phonons while the host framework is responsible for charge carriers transport. Extensive metrology will be used to characterize the crystal and electronic structures of the new compounds. The thermoelectric properties of novel clathrate phases will be studied in a wide temperature range for cooling and waste heat conversion applications.

FY 2014 HIGHLIGHTS

We continued searching for new thermoelectric materials, optimized the syntheses of previously discovered phases, and adjusted the charge carrier concentrations. We have successfully synthesized several clathrates with M-P frameworks, M = Cu and Ni. These compounds exhibit the known clathrate-I framework topology as well as a novel clathrate topology due to the high flexibility of the local coordination of M and P atoms. The charge carrier concentrations in the new phases were adjusted by means of aliovalent substitutions. For example, the clathrate $\text{Ba}_8\text{Cu}_{16}\text{P}_{30}$ exhibits metallic resistivity with holes as the main charge carriers. The charge carrier concentration can be regulated by substitution of Zn for Cu. We investigated the solid solution $\text{Ba}_8\text{Zn}_x\text{Cu}_{16-x}\text{P}_{30}$. The incorporation of Zn atoms resulted in significant structural rearrangements in the framework. For materials with $x=2$ crystallize in the cubic substructure where each framework position is jointly occupied by Zn, Cu, and P atoms. Zn and Cu are neighbors in the periodic system and cannot be distinguished by means of X-ray diffraction techniques. To determine the exact distribution of these elements across the clathrate framework, we collected high-resolution time-of-flight neutron powder diffraction data on representative samples. Analysis of neutron diffraction data indicates that in the cubic disordered phase, Cu and Zn are uniformly distributed over the framework positions. We also performed a search for clathrate-like compounds containing rare-earth cations. Several new phases in the La-Cu-P and La-Zn-P systems have been synthesized and structurally characterized. Both the Cu-P and Zn-P frameworks are very flexible and are able to accommodate different amounts of La cations. In all of the compounds produced, the coordination number of La is typically 14-18, which is smaller than in conventional clathrates.

Biaxiality in Nematic and Smectic Liquid Crystals

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Funding: \$350,000 (2014)

PROGRAM SCOPE

The project's goal is to understand the phenomena of biaxiality and its origin in nematic (N) and smectic liquid crystals (LCs). Known and newly synthesized compounds will be investigated to establish the role of molecular structure and symmetry in the formation of stable biaxial LC phases. A team of five interdisciplinary researchers are probing the biaxiality in the nematic and smectic phases using micro-Raman spectroscopy, x-ray scattering, fluorescence confocal polarizing microscopy, and dielectric permittivity augmented by *ab initio* density functional theory simulations. Specific objectives of the project are: (1) Synthesis of New LC Materials: An important component of the project is the synthesis of (a) bent-core molecules having (i) 5- and 6-membered rings and different terminal/linkage groups, (ii) a chiral center, and (iii) terminal groups replaced with calamitic moiety to form the biaxial phases, and (b) the calamitic mesogens with different aromatic cores and the ratio of siloxane/fluoroalkyl to hydrocarbon segment lengths. DFT simulations will be used to design/improve the molecular structures and stability to obtain the desired properties. (2) Phase Diagrams and Physical Properties: Phase diagrams of new compounds will be determined to test the theoretical predictions, e.g., existence of the Landau point, phase boundary between the isotropic, the uniaxial, and the biaxial phases, and the precise molecular organization; orientational and positional orders in the phases of interest. (3) Biaxial Order and Defect Textures: The uniaxial and biaxial order parameters and the effect of biaxiality on elastic constants and viscosities of LC phases, statics and dynamics of topological defects in both the uniaxial and biaxial N phases will be measured. The project will significantly advance our ability to predictively design mesogens with desired phases and physical properties.

FY 2014 HIGHLIGHTS

- A total of twenty new mesogens ranging from bent-core, hybrid, to calamitic were synthesized to understand the molecular features that give rise to unique phases such as the twist bend nematic and smectic phases with minimal layer shrinkage in the SmC phase.
- Bent-Core analogs of the calamitic mesogens with similar terminal groups were synthesized and found to form the corresponding de Vries smectic and heliconical twist-bend nematic. This result strongly suggests the terminal groups' chemical properties are most important in the formation of these phases.
- Orientational order parameters, molecular distribution function, defects, and dynamics were investigated followed by molecular dynamic simulation using density functional theory with tight binding. Our results provided significant insight into the structure and defect dynamics of de Vries smectic, chromonic, and elastomer main chain liquid crystals.
- A new technique, differential dynamic microscopy, was developed and applied to measure viscoelastic properties of the nematic phase in several systems.
- The project activities led to the publication/submission of 18 peer-reviewed papers, eight plenary/invited presentations at international professional meetings, and nine contributed conference presentations.

Symmetry Breaking for the Synthesis of Nanostructured Porous Materials

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Funding: \$244,000 (2013-2014)

PROGRAM SCOPE

The overarching theme of this program is to develop, understand, and deploy new methods for sorbent synthesis. Porous solids are a ubiquitous class used in chemical manufacturing, water purification, and environmental remediation. Many of these applications are highly energy intensive and the development of better sorbents holds the potential to reduce the energy expended in a process while lowering overall cost. In addition, the development of new high performance sorbents is critical for emerging technologies such as hydrogen/methane storage and carbon dioxide capture. The particular class of sorbents that form the basis of this program are microporous coordination polymers (MCPs). Built from organic and inorganic components, the potential exists to combine the best attributes of established materials such as zeolites and carbons. Nonetheless there have been challenges associated with deploying these materials commercially. The basic science this program strives to understand and control is the self-assembly events that lead to MCP formation. This is a particularly attractive area to exploit because a given set of components can assemble in different arrangements to yield properties that differ vastly. By controlling assembly more nimbly, targeted properties can be optimized. The specific methods to be employed as control elements are spatio-temporal manipulation through a networked reactor system and polymer-induced heteronucleation; these methods have met with considerable success in several other materials synthesis problems but remain almost unexplored in MCP synthesis. In a second major aspect of the project, methodology for the assembly of organic polymers on the outer surfaces of MCPs will be developed and deployed. This is a potentially general approach for making MCPs better suited for large scale use in gas storage, separations, and catalysis by manipulating properties ranging from the mechanical stability to kinetic selectivity for gas sorption.

FY 2014 HIGHLIGHTS

Formation of MCPs by existing synthetic methods relies on secondary building unit (SBU) assembling with organic linkers. The SBU assembles dynamically whereas the linker is relatively static. However, if the ligand structure can change, then competition among assembly of different ligand structures as well as different SBUs has the potential to lead to new structures. We demonstrate this concept using the linker 4-amino-4',4'',4'''-benzene-1,3,5-triyl-tribenzoic acid where the central benzene ring preferentially reacts with terephthalaldehyde and show that formation of different MCPs is achieved by the timed addition of a second reagent. Different addition times yield 2 different phases that are permanently porous: phase I (Surface Area by BET (SABET) = 2820 m²/g) at early delay times and phase II (SABET = 4631 m²/g) at the later stages of addition. Phase I consists of octahedral Zn₄O(O₂CR)₆ SBUs linked together by two amine modified 1,3,5-Tris(4-carboxyphenyl)benzene (BTB) linkers condensed with a single terephthalaldehyde residue via imine linkages whereas phase II is amino functionalized MOF-177. Open space in MCPs is the key to their sorptive properties but also limits aspects of their performance. If pores are too large they offer only a weak attractive potential for gases and residual void space after sorption leads to poor volumetric sorption capacity. To highlight this we have modified naphthalene-2,6-dicarboxylate (NDC), to produce 4-t-butylethynyl-2,6-naphthalenedicarboxylate (tBuNDC) or 4-phenylethynyl-2,6-naphthalenedicarboxylate (PhNDC). The tbutylethynyl or phenylethynyl functional groups occupy part of the pore and serve as additional adsorptive surfaces. Moreover, these functional groups prevent the cubic structure from self-interpenetration. This tuning allows the excess volumetric uptake of methane at room temperature to be increased by as much as 25% compared to the unfunctionalized parent MCP.

Synthesis of Molecule/Polymer Based Magnetic Materials

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Funding: \$237,000 (2014)

PROGRAM SCOPE

New discovery of new materials exhibiting the technologically important property of bulk magnetic ordering as well as those combining magnetism with other technologically important properties (e.g. electrical, optical, and mechanical) is the research focus that is based on the design/synthesis/characterization/exploitation of organic-based magnets (OBMs) using Earth abundant elements. These materials are crucial for future electronic/-photonic devices, especially due to the need to replace rare earth critical materials with Earth-abundant elements, and for reduced energy consumption and environmentally friendlier processing and disposal. We are expanding the $M^{II}(TCNE)_{3/2}I_{3/2}$ (TCNE = tetracyanoethylene) by replacing the anion with triflate by a new post-synthetic modification, as well as making new high T_c V-based magnets via a different route using new iodide-based V(II) compounds. The controlled formation of high T_c $V(II)_x(V(III)_{1-x})[Cr(CN)_6]$ as a function of x are sought via the preparation and controlled use of high purity V(II) and V(III) sulfates. Co-based TCNE magnets have been elusive, with most attempts forming only paramagnetic materials. Nonetheless, we have succeeded in preparing an example with a 66 K T_c , which is being studied.

FY 2014 HIGHLIGHTS

Among several results, the most intriguing is the formation of a Co-based TCNE complex that has a T_c of 66 K that is much higher than any other related Co material - the detailed identification of the composition and magnetic behavior is in progress. Also, albeit not a main-stream project we made $[NMe_4]_2[TCNE]_2$ that exhibits a new type of long (3.04 Å) multicenter CC bond. It has nominal C_2 symmetry and 12 sub-van der Waals interatomic contacts <3.3 Å, and differs for the more common eclipsed D_{2h} π -[TCNE] $_{22}$ - dimer possessing a 2e-/4c bond as it has a 2e-/6c bond. It has diamagnetic ground state with a thermally populated triplet excited state 1400 cm^{-1} above the ground state.

Ion Association for Materials Development

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Funding: \$160,000 (2014)

PROGRAM SCOPE

This project on one level is directed towards advancing polyoxometalate (POM) chemistries, of group V and open-shell transition metals. More broadly, we seek to understand the relationship between

aqueous phase cation-anion association, the solubility behavior of POM salts, and exploiting cation-anion association to stabilize and capture elusive POM compositions and geometries. The POMs of this study provide a unique opportunity due to anomalous solubility behavior. That is, conditions of maximum ion-association correlate with highest solubility. Foundationally, we endeavor to provide a more global understanding of solubility and ion-association in aqueous media, beyond POM chemistry. This work will impact design of materials obtained from aqueous media by exploiting counterion association: both POM-based materials and other metal oxide materials. In addition to synthesis, major experimental techniques include X-ray scattering, multi-nuclear and multi-dimensional NMR, and conductivity. Since the Nb and Ta POMs featured in this study present a solubility trend with their counterions that provides highest solubility where ion-pairing is most prevalent (opposite trend to the tungstates and molybdates), we have an ideal and unique situation to probe the aqueous phase characteristics that define solubility as it relates to ion-association. As part of this inquiry, we are expanding the system of mixed niobate-tungstate POMs to create a series which spans the end-member solubility behaviors to pinpoint reversal in behavior. These series ranging from normal to anomalous solubility behavior will also be explored by thermodynamics of dissolution and computational studies. More broadly, we endeavor to provide guidelines to universally predict solubility behavior and ion-association of any cation-anion assembly in water. The open-shell transition metals have thus far eluded substantial development, and new insights will be gained through understanding counterion effects.

FY 2014 HIGHLIGHTS

Major highlights include 1) understanding differences between aqueous tantalate and niobate clusters, based on their counterion-association behavior in water, 2) detailed characterization of cesium hexaniobate, the workhorse of these studies, and 3) a significant advancement in iron-oxo cluster chemistry. These are discussed briefly below. [1] In a recent publication, (Contrasting ion-association Behaviour of Ta and Nb polyoxometalates Fullmer *et al*, Dalton Transactions, 43(41), 15295, 2014) we present a detailed X-ray scattering study that provides an understanding as to the difference between the chemistry of Nb and Ta in water, based on the behavior of their counterion association. More broadly, this study delineated the relationship between acid-base and counterion behaviors of metal oxides in water. [2] Cs hexaniobate is the POM cluster-salt with the highest solubility and highest counterion-association, and thus has been the focus of many early studies on this project. We have carried out both aqueous and molten salt thermochemistry on Cs, K and Li hexaniobate. The aqueous thermochemistry revealed a much greater concentration dependence on enthalpy of dissolution, which indicated dissolution without complete dissociation is prevalent. This in turn suggests the key to anomalous solubility lies in close association of counterion-cluster, even when dissolved in water. [3] We have isolated the iron-Keggin ion from water, a cluster considered the molecular building block of iron oxide materials such as ferrihydrite. This specie is a long-sought synthon of geochemists, but has never been captured due to its high reactivity in water. We were able to isolate it by first recognizing that the iron Keggin-ion is a highly-charged polyoxoanion rather than the presumed polyoxocation, and by providing equally highly-charged countercations. This manuscript, 'Capture and manipulation of the elusive iron-oxo Keggin ion in water', is currently in review in Science.

EARLY CAREER: Elucidating the Determinants of Alkali Ionic Conductivity in Oxide and Sulfide Frameworks

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Funding: \$750,000 (2014-2018)

PROGRAM SCOPE

The facile conduction of alkali ions in oxide and sulfide host structures is of critical importance in energy storage. Today, the dominant form of energy storage in portable electronics, and increasingly in automotive applications, is the rechargeable alkali-ion battery, a device that functions entirely on the basis of the reversible transport of alkali ions. The Li^+/Na^+ conductivity of a cathode (typically a transition metal oxide) has a direct influence on the rate capability of a Li/Na-ion battery. Alkali conductivity is arguably of even greater importance in the solid oxide and sulfide electrolytes currently being investigated for high safety, all-solid-state batteries, where the diffusion length scales are significantly larger than in the electrodes. This project will elucidate the structural and chemical factors determining alkali conductivity in oxide and sulfide frameworks using large-scale first principles calculations and topological analysis. We will approach this problem through a series of detailed investigations into prototypical structures and chemistries, as well as a broader study carried out over a large number of materials using data mining techniques. The ambition of this project is to go beyond mere screening of materials and acquire the insights necessary to achieve true “reverse design” capability to build high alkali conductivity structures from constituent anion frameworks, cation chemistry, and topology design.

FY 2014 HIGHLIGHTS

The focus of FY 2014 has been on the development of the necessary software infrastructure and scientific methodologies to support automated computational investigations of alkali conductivity in materials. For this effort, we have adopted known high conductivity superionic conductors, such as the $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ material, as test structures. Computations of the conductivity of such fast conductors converge fairly rapidly, and they therefore useful for testing of infrastructure and methods. A robust computational framework has been developed to enable the efficient conduct of automated weeks-long AIMD simulations using resources with limited wall-times, and is currently applied to the study of several cathode and electrolyte chemistries.

EARLY CAREER: Measuring the Importance of Valence to Chemistry of Nanocrystal Surfaces

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Funding: \$150,000 (2014)

PROGRAM SCOPE

The goal of this project is to understand and control the interplay between nanocrystal stoichiometry, surface ligand binding and exchange, and the optoelectronic properties of semiconductor nanocrystals in solution and in thin solid films. We are pursuing three research directions with this goal in mind: 1) We aim to characterize nanocrystal nonstoichiometry and its influence on the number of L-type and X-type binding sites, the thermodynamics of ligand binding, and the kinetics and mechanisms of ligand

exchange. 2) We aim to develop a quantitative understanding of the relationship between surface ligand passivation and photoluminescence quantum yield. 3) We aim to develop methods to replace the organic ligands on the nanocrystal with halide ligands and controllably deposit these nanocrystals into thin films. Electrical measurements on these films will make it possible to evaluate the effect of the nonstoichiometric ligand layer on surface passivation and internanocrystal electronic coupling.

FY 2014 HIGHLIGHTS

We recently discovered a new surface passivation mechanism that involves the reversible binding of metal complexes to the nanocrystals surface. Using nuclear magnetic resonance spectroscopy we demonstrated that metal carboxylate and metal halide complexes reversibly bind to nanocrystal surfaces. A dramatic relationship between the photoluminescence quantum yield and the coverage of the metal ion complexes was observed. This is one of the first quantitative measures of the relationship between ligand coverage and photoluminescence quantum yield. A second highlight comes from nanocrystal thin films prepared using a carboxylate for halide ligand exchange procedure developed in earlier years of the project. Halide terminated cadmium selenide nanocrystal inks were cast from solution and annealed to eliminate weakly bound organic ligands and obtain conductive thin films. Field effect transistor measurements demonstrated record high electron mobilities. Grazing incidence X-ray scattering measurements and electron microscopy allowed us to correlate the nanocrystalline structure to the transport characteristics and unambiguously demonstrated that high mobilities can be obtained within a nanocrystalline film.

Activation of Hydrogen under Ambient Conditions and Unusual Element Hydride Reactivity by Main Group Molecules

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Funding: \$170,000 (2013-2014)

PROGRAM SCOPE

The main theme of this project is the investigation of the reactions of small, important molecules such as hydrogen, olefins, alkanes, amines, isocyanides, carbon monoxide, carbon dioxide, and related species, with main group element compounds. The reactivity of the compounds arises from the presence of both occupied and unoccupied frontier orbitals, which are separated by modest energies of four electron volts or less. The reactions generally occur by a synergic route that involves a push-pull redistribution of electron density that facilitates bond making and breaking. The conditions for reaction reversibility are determined by the energy and symmetry of the molecular energy levels in the compounds, which can be manipulated by changing the electronic and steric properties of the substituents. In principle, the information from these studies can be used to design inexpensive catalysts for fundamental organometallic reactions based on earth-abundant elements, rather than on rare and expensive noble metals. The major focus is on compounds of the elements silicon and aluminum, which are the second and third most abundant elements in the earth's crust. Unfortunately, there are few stable low-coordinate silicon and aluminum compounds with suitable frontier orbital properties for reversible small molecule binding. A program is underway to synthesize low-valent and/or multiple-

bonded derivatives of these elements with a range of different substituents. The synthesis and reactivity of small molecular clusters of these elements with reactive exposed atoms is also being investigated. In the clusters, the coordination of their constituent elements can resemble that of the surfaces of the pure elements, which generally possess highly reactive surface atoms that interact readily with small molecules. The clusters also offer multiple coordination sites for synergistic reactions.

FY 2014 HIGHLIGHTS

Over the past year, work has concerned a variety of topics relevant to the proposal theme. The first reversible complexation of ethylene by a silylene under ambient conditions was studied and the energetics of the reaction were determined. It was shown that the silylene also reacted readily with a variety of substituted alkynes, but not with substituted alkenes, except for conjugated alkenes. A diarylgermylene was shown to react reversibly with white phosphorus at room temperature. A cage germanium-phosphorus compound was formed and characterized spectroscopically and structurally. Photolysis in toluene resulted in regeneration of the germylene and phosphorus. It was shown that the reaction cycle could be repeated up to ten times with little decomposition. In addition, diarylgermylene or stannylene was shown to insert readily into a phosphorus-hydrogen bond of phosphine to generate primary phosphide products. In anticipation of their use as synthons, four bulky primary organoalanes were synthesized and characterized. They were shown to react with ammonia and phosphine to give primary amido alanes or cages with aluminum-phosphorus frameworks. The primary alanes were also reacted with alkenes and alkynes. The latter readily underwent a cis-addition to the Al-H moiety under mild conditions. The ready addition to both terminal olefins and alkynes was attributed to the bulky aluminum substituent, which generated high concentrations of the more reactive unassociated alane. An inverse relationship between the size of the alane substituent and reactivity was established experimentally. The reaction of methylisocyanide with a diarylgermylene afforded isocyanide coupling/oligomerization through carbon-carbon bond formation. Investigation of the reaction mechanism showed that the initial step involved isocyanide complexation, followed by sequential migratory insertion into the germanium carbon bond and subsequent carbon-hydrogen bond activation.

Molecular Processes Underlying the Structures and Assembly of Thin Films and Nanoparticles at Complex Interfaces

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Funding: \$260,000 (2014)

PROGRAM SCOPE

Over the past few decades there has been a tremendous growth in our molecular level understanding of adsorption processes at a variety of solid surfaces. One remaining frontier of discovery is the interface between water and a hydrophobic fluid, an interface that is ubiquitous in the environment, our bodies and a wide range of industrial and commercial products. Our studies explore some of the most fundamental issues that contribute to the adsorption, transport and assembly of macromolecules at this dynamic, complex and important fluid interface. Such issues include understanding how factors such as adsorbate hydrophobicity, charge, water solvation, molecular rigidity, metal-ion complexation and

solubility play a role in the adsorption and assembly process. The first set of studies are designed to examine these issues on adsorbates that range in complexity from simple charged polyelectrolytes (PEs), to polymers of increasing molecular charge and structural complexity, to mixtures of PEs and surfactants that are known to act synergistically, to the structure and assembly of peptoid nanosheets and nanoparticles at this interface. The second set of studies has involved studying the assembly of peptoid nanosheet assembly at the oil/water interface. The fundamental insights sought from these oil/water (O/W) studies underpin some of the most unknown and important areas of interfacial science today. Our approach uses a combination of thermodynamic measurements (surface tension), surface spectroscopy (vibrational sum frequency spectroscopy) and molecular dynamics. The vibrational sum frequency spectroscopic technique that we use is ideally suited for such interfacial studies of molecular assembly at the O/W interface.

FY 2014 HIGHLIGHTS

(1) Polyelectrolyte studies: Whether or not a charged macromolecule remains solvated or adsorbs to the interface between two immiscible fluids depends on a variety of complex factors. Ions, in particular, have the capability of affecting the degree of macromolecular hydrophobicity through charge screening as well as through Hofmeister series effects. In these studies we have used sum frequency spectroscopy and interfacial tension measurements to probe the roles of ions in the oil-water interfacial behavior of a model carboxylic acid-containing macromolecule. Specifically, the structure, conformation, and extent of carboxylate-cation interactions of poly(methacrylic acid) at the carbon tetrachloride-water interface was deduced as a function of CaCl_2 and KCl ionic strength. Additionally, the role of polymer backbone in interfacial behavior is explored through tacticity studies. Results show for the first time that macromolecular charge screening is an important factor in the induced adsorption of the isotactic isomer of poly(methacrylic acid) under solution conditions when it is not strongly surface active, yet does not affect the behavior of the syndiotactic isomer. Additionally, while the salting-out effect does not appear to play a strong role in induced adsorption, there is a balance between polymer salting-in and charge screening with excess calcium. (2) Peptoid Studies Peptoid nanosheets are a recently discovered class of two-dimensional nanomaterials that form from the self-assembly of a sequence specific peptoid polymer at the air-water interface. In our recent studies we have found that the oil-water interface provides another opportunity for growth of these unique and highly ordered peptoid sheets. We have found that nanosheets formed at this interface are highly ordered and that the reason for this is due to electrostatic interactions between charged moieties, namely carboxylate and ammonium residues on the peptoids.

Research Project on the Recruitment Retention and Promotion of Women in the Chemical Sciences

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Funding: \$180,000 (2014)

PROGRAM SCOPE

Committee on the Advancement of Women Chemists (COACH) is a grass-roots organization working to expand its highly successful nationwide efforts at increasing the number, retention and success of

women and minorities in STEM fields. Started in 1998 with an initial focus in the field of chemistry, its programs and impact now extends across the STEM disciplines. Basic Energy Sciences (BES) of the Department of Energy was the first federal agency to recognize the importance of COACH activities and to provide funding for its efforts since 1998. This initial and continued funding for its research on workforce building activities has been critical to the continued success of the organization. Today COACH is widely recognized nationwide for its innovative programs that continue to be adopted by other organizations and institutions, and its high degree of impact on women scientists and institutional administrators that have participated in its programs. BES funding has been the primary supporter of the research arm of COACH. The DOE sponsored research has been a critical element in the evaluation, planning and implementation of nearly all COACH programs.

FY 2014 HIGHLIGHTS

COACH conducted surveys at the following workshops: • American Chemical Society Spring workshop – Jr & Sr. Faculty, Dallas, TX • American Chemical Society Fall workshop – postdoctoral associates, San Francisco, CA • Argonne National Labs – Faculty • Society for the Advancement of Chicanos and Native Americans in Science conference – graduate students, postdoctoral associates, faculty • National Organization for the Professional Advancement of Black Chemists and Chemical Engineers – graduate students, postdoctoral associates, faculty Each survey is a powerful tool in learning more about participant’s career concerns, coping skills, achievement and mentoring; both in their early career and in their current position, how they adapt to career concerns that are always changing (based on the skills learned at the COACH workshops) and how we can offer new skills that the participants need. The results are extremely satisfying in showing the powerful impact that these workshops are having on our participants as they report positive outcomes through follow up emails and correspondence with our facilitators and the COACH office. Two publications based on the surveys are written, one in progress and one has been submitted for review.

Programming Function via Soft Materials

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Funding: \$1,607,000 (2014)

PROGRAM SCOPE

The overarching goal of the proposed program of collaborative research is to develop, understand, and apply in energy-relevant contexts new classes of responsive materials with functionalities that derive from and/or exploit structural dynamics from the nanometer to mesoscopic to continuum scale. The cluster has established a unique enabling vision for such materials that embraces the dynamically

reconfigurable 3-dimensional organization of building blocks into architectures that facilitate ion and electron transport and the harvesting of mechanical energy, with potential for broad utility in advanced energy applications. To achieve this goal we will utilize materials of diverse chemistry in a broad range of organizations (amorphous, crystalline, soft organic, hard inorganic) that are designed to allow programmed reversible transformations between equilibrium and nonequilibrium states with qualitatively different properties. Our cluster's vision for Programming Function via Soft Materials integrates two tightly connected core areas: 1. Reconfigurable and Dynamic Assemblies, and 2. Responsive 3D Mesoscale Networks. As elementary units we will employ function-encoded colloids, nanoparticles, large mesh fibrillar gels, deterministically fabricated networks, and their hybrid mixtures. In addition, we will employ top-down methods to create larger scale systems with a 3-dimensional spatial organization of the material components engineered to provide useful functional behaviors. The scientific and technological implications of the cluster's research will provide new approaches to challenging problems in basic energy science including energy harvesting, transport and storage. To achieve these goals the cluster has brought together a team of recognized world-leaders in complex materials synthesis and processing, characterization, theory and modeling, and materials design, integration and fabrication, organizing their efforts into two synergistic thrusts.

FY 2014 HIGHLIGHTS

Our cluster reported new discoveries in the design and assembly of colloid large-mesh fibrillar polymer gel composites, as a first step in creating dynamically and reversibly reconfigurable percolated networks. Underpinning this work, new optical characterization methods, and a microscopic theory of equilibrium colloidal assembly and electrical conductivity based on using fibrillar polymer networks as templates were developed. Continued strides were made in reversible-deactivation fibril assembly, a possible route to forming structurally well-defined polymer filaments with narrow polydispersity. Synthetic strategies for mechanically optimized objects, both colloids with shape bistability and high energy density battery electrodes with minimized plastic strain upon cycling, were developed. Mechanical modeling was used to understand the properties of these systems. Mechanically optimized silicon battery electrodes were found to have significantly increased cycle lifetimes compared to conventional electrode designs. Complex, 3D mesoscale networks were formed by exploiting the geometric transformation via compressive buckling of 2D micro/nanostructures into extended 3D layouts. Demonstrations include experimental and theoretical studies of more than forty representative geometries, from single and multiple helices, toroids and conical spirals to structures that resemble spherical baskets, cuboid cages, starbursts, flowers, scaffolds, fences and frameworks, each with single and/or multiple level configurations. Modeling of electric fields within such structures was performed, and studies of their dynamical behavior are ongoing. The developed process can be implemented with any substrate capable of controlled, large-scale dimensional change. It expands and complements the capabilities of other approaches in 3D materials assembly, and suggests many new possibilities for achieving sophisticated classes of 3D electronic, optoelectronic, and electromagnetic devices.

EARLY CAREER: Dielectric Ceramics in Nanosheet Form

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Funding:	\$150,000 (2014)

PROGRAM SCOPE

Nanosheets are characterized as being freestanding nanomaterials from one to several monolayers thick and up to tens of micrometers in lateral dimensions. The nanosheet morphology has several unique features that put it at the frontier of materials development, foremost the fact that nanosheets can combine remarkable, quantum effect-derived properties with large surface areas and the advantages of solution-based manipulation methods. To date, well-defined nanosheets have been derived from lamellar materials via exfoliation processes; examples include selected perovskites, various transition metal oxides and chalcogenides, hexagonal boron nitride, and graphene. We are interested in materials for energy applications that go beyond these examples, specifically ternary oxide ceramics. The important initial challenge is that there is no bulk precursor that can simply be exfoliated to provide nanosheets of these materials. However, when this preparative hurdle is surmounted, these nanosheets will provide an opportunity to better understand the properties of complex oxide ceramics at a size regime down to one monolayer, as well as allow us to study the roles of surface functionalization and interface interactions. Our approach in this area of two-dimensional ceramic nanomaterials encompasses synthesis, characterization, and deposition methods.

FY 2014 HIGHLIGHTS

The first step is to prepare dielectric ceramics as nanosheets, a non-natural form of these materials. Our innovation is to apply template-based and topotactic chemical transformations to pre-existing nanosheet starting materials. We have focused on two classes of ternary oxide materials that have well-characterized ferroelectric properties: the titanate-based perovskites ATiO_3 ($A = \text{Ba, Sr, Pb}$) and the bismuth-based Aurivillius materials Bi_2MO_6 ($M = \text{Mo, W}$). Our synthetic studies to produce ATiO_3 nanosheets have focused on the topotactic conversion of titania- or titanate-containing nanosheet precursors. For example, we have developed direct TiO_2 (B) nanosheet to BaTiO_3 nanosheet conversion chemistry. A large part of this effort has involved an in-depth study of the mechanism of BaTiO_3 nanosheet formation. Structure analysis of BaTiO_3 nanosheets by Raman spectroscopy and synchrotron X-ray diffraction reveal that the material is tetragonal at room temperature, which is a key prerequisite for ferroelectric properties. Recent piezoresponse force microscopy (PFM) measurements with collaborators (Prof. Matt Dawber, SUNY Stony Brook, Physics) have shown that BaTiO_3 nanosheets show a clear piezoresponse at room temperature. In the Bi_2MO_6 system, we developed a double nanosheet template route to preparing high-quality Bi_2WO_6 and Bi_2MoO_6 nanosheets. The most successful reactions involve two nanosheet materials under hydrothermal conditions, such as surfactant-free cesium tungstate $\text{Cs}_4\text{W}_{11}\text{O}_{36}^{2-}$ nanosheets with bismuth oxide-based $[\text{Bi}_6\text{O}_6](\text{OH})_3(\text{NO}_3)_3$ nanosheets that are generated *in situ* from $\text{Bi}(\text{NO}_3)_3$, or with isolated $[\text{Bi}_6\text{O}_6](\text{OH})_3(\text{NO}_3)_3$ nanosheets. We characterized the band gaps of Bi_2MO_6 nanosheets compared to other nanomorphologies and bulk material, an important factor in its well-known photocatalytic properties, and discovered that Bi_2WO_6 is reversibly chromic with respect to both UV irradiation and lithium intercalation.

Hybrid Halide Perovskites: Novel Materials with Contraindicated Properties

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Funding: \$468,022 (2014)

PROGRAM SCOPE

We have worked on the synthesis and characterization of the hybrid organic/inorganic germanium perovskite compounds, $AGeI_3$. The systematic synthetic study of this reaction system led to the isolation of 6 new inorganic semiconductors by incremental variation of the A organic cation. Using $CsGeI_3$ (1) as a reference compound we have prepared the methylammonium, $CH_3NH_3GeI_3$ (2), formamidinium, $HC(NH_2)_2GeI_3$ (3), acetamidinium $CH_3C(NH_2)_2GeI_3$ (4), guanidinium, $C(NH_2)_3GeI_3$ (5), trimethylammonium, $(CH_3)_3NHGeI_3$ (6), and isopropylammonium, $(CH_3)_2C(H)NH_3GeI_3$ (7), analogues. The crystal structures of the compounds were solved and refined and they are classified based on their dimensionality with 1-4 forming 3D perovskite frameworks and 5-7 1D infinite chains. The binary compound GeI_2 (8), prepared under the same synthetic protocol, has a layered 2D structure and lies between the two structural families. Compounds 1-8, with the exception of compound 5, crystallize in strongly polar space groups, a property that can be attributed to the tendency of the Ge^{2+} ion to form pyramidal $[GeI_3]^-$ rather than octahedral $[GeI_6]^{4-}$ building blocks in the solid state, in contrast with the tendency observed in the heavier iodometallates. Complementing this work, we have prepared a number of Bi-based halide compounds of the general formula $A_3Bi_2I_9$ where A is either an alkali metal cation or an organic amine-derived mono cation. The structures and phase transitions of some of these and their optical properties have been studied. To study the behavior of charge carriers in these materials, we have begun to set-up a transient THz system to study the lifetime and spectral features of photogenerated carriers. We have also prepared the proposed zwitterionic molecule that can act as both electron and hole transporter interface molecule, and are now incorporating these into devices.

FY 2014 HIGHLIGHTS

Some of the highlights obtained so far include a careful DFT study of valence and conduction band absolute positions of PbI_2 and $APbI_3$ compounds with different dimensionalities of structures that has been published in the Journal of Physical Chemistry. The chemistry of many new Ge, Sn, and Bi compounds has been studied as well.

Computation-Guided Synthetic Strategies for Nanocomposite Electrode Structures Designed to Probe Critical Size Effects on Charge Storage and Transport

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Funding: \$250,000 (2014)

PROGRAM SCOPE

One of the premises of this project is that materials with high theoretical capacities for lithium ion storage may serve as active electrode materials for electrical charge storage devices such as lithium ion batteries (LIBs) even if they are poor electronic or ionic conductors, given that the materials are present

as nanoparticles and that they are in good electronic contact with a conducting phase. To achieve efficient charge storage and transport in such materials, it is necessary to control size and morphologies of active material particles and their distribution in the conductive phase. During this project period we focused on two particular systems: titania/carbon nanocomposites for anodes in LIBs and the lithium zirconate (LZO) platform for potential novel cathode materials. For the former, we investigated the influence of the source of carbon and titania on the nanocomposite to improve control over the carbon:titania ratio, nanoparticle size, and titania distribution in the carbon phase. These parameters were correlated to electrochemical properties. The LZO platform is attractive because of the layered structure in some phases that allows for cation intercalation/deintercalation and because of its high theoretical specific capacity for charge, which exceeds that of current commercial cathode materials. Several challenges must be overcome for LZO electrodes, related to the low conductivity of LZO and its high charging potential. These challenges are addressed through the development of syntheses of materials with small grain size, some of which directly incorporate LZO in a conductive carbon phase. Furthermore, dopants are introduced into the active material to enhance electronic conductivity, ionic conductivity, or both. We have made tremendous progress in understanding how to manipulate grain size and electrochemical properties of the LZO-based system. Much of this progress has been guided by computational insight.

FY 2014 HIGHLIGHTS

We demonstrated that by using a polymeric template with mixed precursors for carbon and titanium complexed by different ligands, it was possible to position titania nanoparticles either at the interface of pores or embedded within a carbon matrix. The relative placement influenced the capacity of the material to store lithium ions and depends on the interactions (relative polarity) of the complexed titanium precursor with the carbon precursor and the template surface. The carbon content is also affected by the ligand. Embedding titania within carbon limits grain growth, whereas surface titania grows nearly unrestrictedly. Excessive carbon limits ion transport, reducing capacity at high charge/discharge rates. These observations are also relevant for other hard templating processes to fabricate nanocomposite electrodes. For the LZO platform several properties were computed, including geometries and electronic structures of delithiated configurations, delithiation energy, and stability of the delithiated materials. Li ion transport mechanisms were explored, and the lowest energy path of Li hopping was identified. Surface effects and doping effects on the electronic structure of the cathodes and the delithiation energy were simulated. This information guided the selection of dopant atoms. Multiple approaches were evaluated to reduce the grain size of LZO particles, shorten diffusion paths through active material and increase electrochemical utilization, including ultrasonic exfoliation, synthesis from nanostructured precursors, synthesis in confinement of carbon phases, and synthesis from sinter-resistant precursors. By correlating grain size with charge storage capacities, we deduced a target size of 5-20 nm crystallites for full utilization. Capacities were enhanced by doping with selected transition metals through providing either defect sites in the structure for improved ion conductivity or through enhancing electronic conductivity.

Electrochemically Smart Bimetallic Materials Featuring Group 11 Metals: In-Situ Conductive Matrix Generation & Its Impact on Battery Capacity, Power and Reversibility

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Funding: \$200,000 (2014)

PROGRAM SCOPE

This research on energy storage is centered on the syntheses and electrochemical studies of new classes of bimetallic energy storage materials. There are three interrelated objectives that we are pursuing. 1) Develop new classes of improved materials based on bimetallic oxides, oxyphosphates and phosphorous-oxides: $M_wM'_xO_z$, $M_wM'_xOP_yO_z$, $M_wM'_xP_yO_z$. The investigation includes a) rational identification of next generation target materials, b) performing detailed chemical and physical characterization of the materials and c) control of the material properties via the synthetic manipulation of the material composition and nanostructure. 2) Conduct electrochemical evaluation of the interrogated materials to determine energy density, electrochemical reversibility, and power capability, under a variety of conditions. 3) Fundamentally interrogate the reduction/oxidation mechanisms of the materials. This program is focused on the synthesis, characterization, electrochemical evaluation of novel bimetallic compounds in three major classes: 1) manganese centered materials, 2) vanadium centered materials and 3) iron based compounds. The research probes the impact of structure and in particular crystallite size on the electrochemistry. A focus on synthetic methods enabling control of physical properties of materials such as crystallite size, surface area, and particle size, as well as chemical composition can result in control of the bulk properties of materials, critical to mechanistic electrochemical studies. Novel low temperature synthetic techniques that provide the ability to control crystallite size along with composition yielding molecular level architectural design capability are developed which enable systematic studies of specific factors as related to their electrochemistry. The studies are supported by mechanistic studies using ex-situ and in-situ measurements.

FY 2014 HIGHLIGHTS

Significant findings in three topic areas were realized in 2014: 1) demonstration of a synthetic method allowing composition and size control yielding 200% increase in delivered capacity, 2) in-situ studies of intact batteries yielding kinetic insight on the formation of the electrochemical reaction front within the cathode and 3) demonstration of reversibility of copper based bimetallic materials yielding nanosized copper which reincorporates into the parent structure. A paradigm for concomitant control of crystallite size and composition of bimetallic composites via co-precipitation was introduced where the direct preparation of a composite of silver ferrite, $AgFeO_2$ and amorphous maghemite, $\gamma-Fe_2O_3$ via nonstoichiometric synthesis was demonstrated. X-ray powder diffraction confirmed systematic variation of crystallite size. The composite nature of crystalline silver ferrite and non-crystalline maghemite was established by Raman and x-ray absorption analyses. The low silver composites exhibited capacities ~200% higher relative to stoichiometric silver ferrite. Our strategy to address low electrical conductivities of cathode materials is designing bimetallic materials that in-situ form an electrically conductive metallic matrix. In-situ energy-dispersive x-ray diffraction enabled three dimensional spatial imaging of intact $Li/Ag_2VP_2O_8$ and $Li/Ag_2VO_2PO_4$ cells. Formation of silver metal during discharge enabled visualization of discharge pathways within the battery cathode. Studies of cells discharged under different rates provided unique insight into the role of rate as a deterministic factor in the reduction mechanism. Synthesis, characterization and electrochemical studies of $Cu_{0.5}VOPO_4 \cdot 2H_2O$ and $Cu_{0.25}MnO_2 \cdot H_2O$ were completed where both materials showed reversible electrochemistry. Formation of copper metal on reduction was not detectable by XRD, but was identified by x-ray absorption spectroscopy providing insight into the reversible reduction mechanisms.

EARLY CAREER: Transition Metal Oxides Spinel Nanomaterials for Supercapacitor Reactions

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Funding: \$150,000 (2014)

PROGRAM SCOPE

This project will focus on the fundamental structure-property relationship of transition metal oxides (TMOs) nanostructures made from liquid phase synthesis with defined morphology, chemical composition and crystalline structure, including faceted simple spinel (e.g., Mn_3O_4) and binary spinel (e.g., $Co_{1-x}Mn_{2-x}O_4$ and $Fe_{1-x}Mn_{2-x}O_4$), and layered TMOs (e.g., MnO_2 , V_2O_5). The hypotheses of our research are: (i) nanosized TMOs will have high specific surface area for ionic conductance; (ii) faceted spinel nanoparticles with higher percentages of reactive and/or stable surfaces will facilitate the fast charge-transfer reaction and long cycle life; (iii) layered nanostructures will provide large interplanar distance for facile cation insertion/extraction. Various analytical tools (electron microscopy, thermogravimetric analysis and XPS) will be used to characterize the structure of TMOs. Cyclic voltammetry and electrochemical impedance spectroscopy analyses (in half-cell), and galvanostatic charge-discharge analyses (in button-cell) will be used for electrochemical characterization. Particularly, through the interplay between novel material syntheses, structural and functional characterizations, and synchrotron-, neutron-based *in situ* X-ray diffraction (XRD), X-ray adsorption (XAS), neutron scattering and pair distribution function (PDF) analyses; the ultimate goal of the proposed research is to provide fundamental understanding of electrode materials for supercapacitors that can store more energy while maintaining a stable electrode/electrolyte interface.

FY 2014 HIGHLIGHTS

We synthesized Mn_3O_4 spinel, and Co- and Ni-doped Mn_3O_4 ($Co_xMn_{3-x}O_4$, $Ni_xMn_{3-x}O_4$, X: 0, 0.2, 0.5, 1, and 3) spinel metal oxide nanoparticles, and V_2O_5 layered nanostructures, and fabricated electrodes for supercapacitor devices and studied their electrochemical performance. We conducted several *ex situ* X-ray and neutron diffraction experiments at ORNL-SNS and ANL-APS, and *in situ* XRD and XAS measurements on V_2O_5 , Co- Mn_3O_4 . Future efforts will focus on understanding the effect of crystalline structure on potential window of the electrochemical devices, and the PDF analyses of X-ray and neutron scattering data.

Mesoscale Photophysical Properties of Anisotropic Hybrid Nanostructure Assemblies

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Funding: \$250,000 (2014)

PROGRAM SCOPE

Hybrid (organic-inorganic) mesoscale assemblies of functionalized anisotropic nanocrystals with tailored shapes and facet-to-facet interactions with conjugated photoluminescent polymers will be investigated in this project. We use shaped noble metal nanocrystals coated with functionalized materials including conjugated polymers and satellite nanoparticles to control their inter-particle interactions as well as light interactions and conversion. Building blocks with different shapes and functionalized facets self-assemble to yield mesoscale structures in a pre-programmed fashion offers a unique opportunity to create hierarchical structures and materials with inherently anisotropic properties such as optical, transport, mechanical, or magnetic depending upon the nature of building blocks. We focus on the plasmonic-mediated changes of the light absorption of core-shell metal-conducting polymers nanostructures which can serve as efficient light-harvesting and converting hybrid materials. Specific objectives include: (1) synthesis of different complex shaped nanostructures (nanocubes, nanoframes, nanocages) from noble metals with well controlled dimensions, shapes, and stability and their functionalization in order to control their assembling ability; (2) fabrication of core-shell hybrid nanostructures with controlled placement of different conjugated polymer shells; (3) comprehensive multi-length scale characterization of microstructure, morphology, thermal, and optical properties of these hybrid nanostructures; (4) directed assembly of these functionalized nanostructures into the organized mesoscale ensembles with controlled interparticle distances via competing interactions of functionalized facets and surfaces. The ability to control light interaction of core-shell, metal-polymer nanostructures is a critical requirement for designing hybrid materials with novel light harvesting and conversion properties for energy materials, catalysts, biosensing, and photonics.

FY 2014 HIGHLIGHTS

Monolayers of polyethylene glycol (PEG)-functionalized gold nanocubes (AuNCs) were fabricated with the separation controlled by the PEG chain length (J. Phys. Chem. C 2014, in print). The alignment of the AuNRs resulted in a strong longitudinal localized surface plasmon resonance (LSPR) when excited by polarized light. A variable surface pressure allows continuous size gradient of nanocubes with poly(isopropylacrylamide) shells with variable interparticle coupling (ACS Nano 2014, 8, 9410). On the contrary, the ensembles of nanoparticle arrays on periodic wrinkled templates show strong plasmonic coupling due to minute interparticle spacing of 2 nm resulting in well-defined plasmonic modes, such as resonance splitting and multiple radiant modes (NanoLett. 2014, 14, 6863). Furthermore, we observed strong plasmonic coupling within aggregates of silver nanocubes on different substrates that lead to a substantial enhancement of the refractive index sensitivity (Particles, 2014, 31, 274). Top down and directed assembly methods such as electron beam lithography and layer-by-layer assembly were exploited to engineer metal-dielectric-metal nanostructures with broadband absorbing properties. Coupling of silver nanocubes and gold nano-gratings mediated by a dielectric polymer spacer with controllable nanoscale thickness results in a large enhancement of light absorption (Adv. Funct. Mater. 2014, 24, 6797). Precise design of optical scattering sites in a 3D stacking yields plasmon resonance modes not observed in common 2D metal nanostructures (J. Phys. Chem. C 2014, 118, 5453). Finally, real time plasmonic tunability was achieved by embedding silver nanocubes into an electrochromic polymer matrix and applying electrical field. A significant reversible plasmon peak shift was observed when the nanocube-polymer layer was electrochemically oxidized due to initiated changes in the refractive index of the polymer matrix as supported by Finite Difference Time Domain (FDTD) simulations (ACS Nano 2014, 8, 6182).

Optical, Electrical and Magnetic Studies of pi-Conjugated Systems

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PROGRAM SCOPE

The thermodynamic limit of organic photovoltaic (OPV) solar cell is ~25% for single-junction cells. So far the world record certified power conversion efficiency (PCE) of OPV solar cells is 10.6%, for a solar cell based on low bandgap (LBG) polymers. Despite aggressive efforts in the past two years, only minor progress in PCE of organic solar cells has been made, and thus game-changing fundamental understanding is critically needed for the next breakthrough in PCE enhancement. This may be achieved by finding new energy transfer pathways that circumvent the loss mechanisms known to exist in organic donor (D)-acceptor (A) bulk heterojunction (BHJ) blends. Consequently, our goal in the present DOE project is to seek, understand and provide new energy transfer processes in polymeric and molecular D-A OPV devices, through a concerted research effort using ultrafast and continuous wave (CW) spectroscopy that include transient magnetic field effect, device fabrication and electrical characterization; and advanced computation via collaboration. Based on the deeper understanding gained by our research progress, new materials and processes will be developed to reduce losses in the basic processes of charge photogeneration, transport, and collection in OPV cells that will boost the device PCE.

FY 2014 HIGHLIGHTS

Our approach to fulfill this goal has involved understanding why charge photogeneration at the polymer-fullerene interface with the state-of-the-art LBG polymers is significantly higher than with traditional donor materials. Our recent experimental research indicates that there exist in LBG polymers unusual charge photogeneration channels with yield above that of the normal charge photogeneration channel of singlet exciton (SE) dissociation; which involve either a triplet exciton that results from singlet fission (SF), or a spin-singlet state that is a quantum entangled triplet-triplet (TT) state. These conclusions were reached from novel ultrafast spectroscopy measurements under the influence of an external magnetic field that were completed in our laboratories on pristine and blends based on LBG, which show the ultrafast photogeneration of a novel intrachain TT state that undergoes SF and ionizes at the D-A interface to polaron-pairs. Also sophisticated calculations of ground state and excited state absorptions within correlated-electron models of π -conjugated polymers justify our conclusions. These calculations show that intrachain TT pairs may be readily photogenerated in LBG polymers upon photon absorption, as a result of their intrachain D-A backbone structure.

Linking Metal Ions via Inorganic Click (iClick) Reactions

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

Inorganic click (iClick) is the cycloaddition reaction between a metal-azide and a metal-acetylide providing metal ions linked by a triazolate bridge. This reaction was first elucidated in the Veige laboratories in 2010. The iClick reaction has the potential to transform synthetic methodologies that rely on the controlled linkage of two or more metal ions. Although metallopolymers are versatile and have extensive applications, most notably as light harvesters in photovoltaic devices, these materials are hampered by a limited range of the metal coordination environments, limited synthetic access to regular heterometallic compounds, and limited methods for post-synthetic modification. iClick methodology can afford controllable incorporation of metal ions into a polymer chain with complimentary properties afforded by the ancillary ligands. However, the underlying fundamental chemistry that governs the iClick reaction is unknown. This one-year project aims to determine the scope of the iClick reaction, including a CuI-catalyzed version and extension to tri- and tetra-metallic complexes that will serve as models for future metallopolymer materials. Over the past year we have garnered preliminary results that substantiate iClick chemistry as an effective method to link metal ions. This project delineates experiments that will afford a detailed understanding of the electronic and steric effects of the monomer units that govern this reaction. Our initial target molecules are di- tri- and tetra-metallic compounds, which approximate extended structures and will elucidate how metal ion type and ancillary ligands affect electronic exchange/communication across the triazolate bridge. The goal is to firmly grasp both the advantages and limitations of this new technology to facilitate, beyond this project, the controlled synthesis of one- and two-dimensional metallopolymers and metal-containing networks.

FY 2014 HIGHLIGHTS

The major highlight from the previous project year is that we transitioned the iClick reaction from a reaction that links two and three metal ions, to a reaction that links multiple metal ions to provide metallopolymers and oligomers. This marks the first use of an iClick reaction to form new materials previously unattainable. In one case, we employ iClick to link two Au(I) units together that then self-assemble into rare Au₄ clusters. The Au₄ clusters then, depending on steric constraints from the ancillary ligands, forms oligomers through aurophilic interactions. The significance is that our system is a rare example of oligomer formation driven via gold-gold bonds. Another approach was applied that employs the cycloaddition of an organodiazide to a metal-diacetylide. Setting up a step-growth polymerization, for the first time we demonstrate metallopolymer formation, with in-chain metal ions via iClick. Lastly, we elucidated an alternative iClick reaction that employs the cycloaddition of an isonitrile with an Au-azide to form new tetrazole coordination polymers. These three highlights cement iClick as a versatile method for accessing new materials that feature in-chain metal ions rather than pendant metals attached to a polymer backbone.

Donor-Acceptor Extended Porphyrins as Light Harvester for Solar Energy Conversion

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Funding: \$210,000 (2014)

PROGRAM SCOPE

This funded project is focused on the design, synthesis and characterization of pi-extended porphyrins bearing donor and acceptor groups at the porphyrins beta-positions, as well as the evaluation of these pi-extended porphyrins as light harvesters for dye-sensitized solar-cells (DSSCs). Pi-extended porphyrins possess unique combination of photophysical and electronic properties. These organic materials have great potentials in applications ranging from organic electronics to biomedicines. Due to the very limited synthetic methods, this area remains largely unexplored. We have developed concise and versatile synthetic methods to access a large number of pi-extended porphyrins. The goal of this project is to establish basic understandings of the structure-property-efficiency relationships through systematic functionalization of pi-extended porphyrins.

FY 2014 HIGHLIGHTS

In the year of 2014, we completed the synthesis and characterization of four types of pi-extended porphyrins including linearly conjugated pentacene-fused porphyrin dimers, cross-conjugated quinone-fused dinaphtho[2,3]porphyrins, unsymmetrical push-pull monobenzoporphyrins and push-pull opp-dibenzoporphyrins. The linearly conjugated pentacene-fused porphyrin dimer and the cross-conjugated quinone-fused dinaphtho[2,3]porphyrins display non-typical UV-visible absorptions of either porphyrins or pentacenes/quinones. UV-visible, emission and MCD spectroscopy suggest strong electronic interactions among the multichromophores in the system. DFT calculations revealed the delocalization of the HOMOs and LUMOs spanning the entire dimer and linker assembly. It is notable that the pentacene-fused porphyrin dimer is significantly more stable than both the corresponding pentacene and the heptacene derivatives. Both the unsymmetrical push-pull monobenzoporphyrins and push-pull opp-dibenzoporphyrins exhibit anticipated broadening and red shifting of UV-visible absorptions. An unusual flipping over in magnetic circular dichroism spectroscopy (MCD) of unsymmetrical push-pull monobenzoporphyrins was observed for the first time for porphyrins. We are in the process of measuring cyclic voltammograms (CVs) and other properties for these four types of pi-extended porphyrins. The performance of these porphyrins in dye sensitized solar cells (DSSCs) will also be measured. We expect five to six papers from these results. One article has been published (Chem. J. Eur., 2014, 1-7; selected as a hot paper by the editors). One article has been submitted to Chem. Commun. Two manuscripts are near submission for publication.

Extracting Hot Carriers from Photoexcited Semiconductor Nanocrystals

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Funding: \$210,000 (2013-2014)

PROGRAM SCOPE

This research program addresses a fundamental question related to the use of nano-materials in solar energy -- namely, whether semiconductor nanocrystals (NCs), also called quantum dots (QDs), can help surpass the efficiency limits in conventional solar cells. As is known as the so-called "Shockley-Queisser" limit, the maximum theoretical efficiency of a single-junction solar cell is ~31%. This is because absorption of photons with energies above the semiconductor bandgap generates "hot" charge carriers that quickly "cool" to the band edges before they can be utilized to do work. If instead, all of the energy of the hot carriers could be captured, solar-to-electric power conversion efficiencies could be increased, theoretically, to as high as 66%. Two proposals have been put forward: one increases photocurrent by converting the hot carrier energy to multiple electron-hole pairs; and the other increases photovoltage by capturing the hot carriers. In both scenarios, it is essential to understand charge carriers or excitons significantly above the bandgap. The PI is addressing two questions: How does quantum confinement affect hot carrier/exciton dynamics? How to harvest hot carriers from quantum confined materials, including quantum dots? Understanding hot carriers and excitons in semiconductor materials, including quantum-confined materials, is a necessary step in laying a mechanistic foundation for the application of these materials in solar energy conversion. The second question is specifically related to the potential implementation of the hot carrier solar cell idea. The key to the success of the hot carrier solar cell concept lies not only in the efficient harvesting of hot carriers before phonon relaxation, but also in the possibility of hot carrier – hot carrier scattering and quasi equilibration in the electronic degrees of freedom with realistic concentration of solar radiation.

FY 2014 HIGHLIGHTS

The PI has made two major advances in understanding hot carrier relaxation in the model system in PbSe QDs. The PI has successfully applied femtosecond time-resolved two-photon photoemission spectroscopy for a complete mapping in time- and energy-domains of hot electron relaxation and multi-exciton generation (MEG) dynamics in PbSe quantum dots functionalized with 1,2-ethanedithiols. This experiment led to the discovery of a linear scaling law between the hot electron relaxation rate and its energy above the conduction band minimum. There was no evidence of MEG from intra-band hot electron relaxation for excitation photon energy as high as three times the bandgap ($3E_g$). Rather, MEG occurs in this system only from inter-band hot electron transitions at sufficiently high photon energies ($\sim 4E_g$). More insight into the behavior of hot carriers in PbSe QDs comes from transient absorption experiments. Here, the PI and students have discovered a transient Stark effect imposed by a hot electron-hole pair on optical transitions in PbSe QDs. The hot electron-hole pair does not behave as an exciton, but more bulk-like as independent carriers, resulting in a transient and varying dipole moment which breaks the symmetry of the QD. As a result, we observe redistribution of optical transition strength to dipole forbidden transitions and the broadening of dipole-allowed transitions during the picosecond lifetime of the hot carriers. The magnitude of symmetry breaking scales with the amount of excess energy of the hot carriers, diminishes as the hot carriers cool down, and disappears as the hot electron-hole pair becomes an exciton. Such a transient Stark effect should be of general significance to the understanding of QD photophysics above the band gap. More recently, the PI and students have made a breakthrough discovery on a new class of solar harvesting materials, organic-inorganic lead halide-based perovskites, on charge and exciton trapping, as well as light emission.

Spectroscopy of Charge Carriers and Traps in Field Doped Organic Semiconductors

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Funding: \$290,000 (2013-2014)

PROGRAM SCOPE

The proposed research aims to achieve quantitative, molecular level understanding of charge carriers and traps in field-doped crystalline organic semiconductors via *in situ* linear and nonlinear optical spectroscopy, in conjunction with transport measurements and molecular/crystal engineering. Organic semiconductors are emerging as viable materials for low-cost electronics and optoelectronics, such as organic photovoltaics (OPV), organic field effect transistors (OFETs), and organic light emitting diodes (OLEDs). - Despite extensive studies spanning many decades, a clear understanding of the nature of charge carriers in organic semiconductors is still lacking. It is generally appreciated that polaron formation and charge carrier trapping are two hallmarks associated with electrical transport in organic semiconductors; the former results from the low dielectric constants and weak intermolecular electronic overlap while the latter can be attributed to the prevalence of structural disorder. These properties have led to the common observation of low charge carrier mobilities, e.g., in the range of 10^{-5} - 10^{-3} cm²/Vs, particularly at low carrier concentrations. However, there is also growing evidence that charge carrier mobility approaching those of inorganic semiconductors and metals can exist in some crystalline organic semiconductors, such as pentacene, tetracene and rubrene. A particularly striking example is single crystal rubrene, in which hole mobilities well above 10 cm²/Vs have been observed in OFETs operating at room temperature. Temperature dependent transport and spectroscopic measurements both revealed evidence of free carriers in rubrene. Outstanding questions are: what are the structural features and physical properties that make rubrene so unique? How do we establish fundamental design principles for the development of other organic semiconductors of high mobility?

FY 2014 HIGHLIGHTS

We have carried out transport measurements on ionic liquid (electrolyte) gating of two benchmark organic semiconductors, poly(3-hexylthiophene) and rubrene. The goal of these experiments is to use the giant capacitance of ionic liquids to induce large carrier densities in the organic semiconductors and to explore transport in the high carrier density regime. We find that in the case of P3HT, the mobility becomes high enough at the 3D highest charge densities, near 10^{21} cm⁻³, that the Hall effect can be reproducibly observed. Furthermore, it is clear from extensive resistivity measurements versus temperature that a metallic state in P3HT is approached, though it is not realized likely due to gating induced disorder. In the case of rubrene single crystals, carrier mobilities as large as 4 cm²/V.s are achieved at 2D hole densities of 0.15 charges/rubrene, $\sim 3 \times 10^{13}$ cm⁻². These large mobilities lead to an easily detected Hall signal that verifies the charge density estimated from capacitance-voltage measurements. Furthermore, at optimum carrier densities, the near-onset of metallic behavior is clearly observed for rubrene. Concurrent with transport experiments, we carried out spectroscopic measurements to quantify the density of doping upon the formation of the rubrene/ionic liquid (ion gel) interface. Based on charge modulation FTIR spectroscopy, we discovered that there is an intrinsic doping of the rubrene capacitor with an ionic gel dielectric of $\sim 1.5 \times 10^{13}$ cm⁻² holes (manuscript in preparation).

Such an intrinsic density of doped holes can be removed with a positive gate bias of $V_G = 0.8$ V. These intrinsically doped holes are believed to result from the stabilization of hole carriers at the interface by counter ions (anions) in the ionic gel, a process similar to the trap healing mechanism discovered recently by Podzorov and coworkers. For negative gate bias up to $V_G = -1.0$ V, we find addition hole doping up to $\sim 3 \times 10^{13} \text{ cm}^{-2}$, in agreement with transport.

A Synthetic Strategy to Prepare New Complex Uranium and Thorium Containing Oxides: Predictive Solid State Synthesis of New Composition using Radius Ratio Rules and Materials Discovery Based on Crystal Growth from High Temperature Solutions

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Funding: \$140,000 (2014)

PROGRAM SCOPE

The synthesis of new complex uranium-containing materials and the investigation of their physical properties are of interest and of national importance for identifying new ceramics for long term waste storage, for developing new materials for fuel rod assemblies, and for training the next generation of radiation worker. Achieving these goals will require complex uranium-containing materials with substantially new compositions and structures and the involvement and training of graduate students and postdocs in the synthesis process. However, the preparation and characterization of new oxide compositions is not a trivial undertaking and requires a targeted approach. Our research continues to focus on expanding the boundaries of uranium(IV) and uranium(VI) materials chemistry via two approaches: 1) the targeted synthesis of complex oxides with compositions and structures predicted by radius ratio rules and 2) the crystal growth of new complex uranium oxides from high temperature solutions as an effective method for materials discovery. A third approach, 3) the mild hydrothermal crystal growth method, enables us to obtain large high quality crystals of uranium (IV) containing fluorides via an in-situ reduction step. In all cases, we perform the structural characterization of these crystals and characterize the physical properties of the new materials synthesized.

FY 2014 HIGHLIGHTS

During the past year we focused on a successful area of crystal growth that yielded new ternary U(IV) containing fluorides and a new series of U(VI) containing oxy-chlorides. We also began to explore the uranium silicate phase space that has yielded very promising results so far. We relied extensively on the use of mild hydrothermal reactions for the synthesis of single crystals of new binary, ternary and quaternary fluoride phases and on the use of high temperature fluxes for the preparation of ternary and quaternary oxides and oxychlorides. We developed robust synthetic methodologies that enabled us to synthesize and characterize numerous new uranium-containing phases including (1) fluorides: $\text{Na}_4\text{MU}_6\text{F}_3\text{O}$ ($M = \text{Mn}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{and Zn}^{2+}$), $\text{Na}_3\text{MU}_6\text{F}_3\text{O}$ ($M = \text{Al}^{3+}, \text{Ga}^{3+}, \text{Ti}^{3+}, \text{V}^{3+}, \text{Cr}^{3+}, \text{Fe}^{3+}$), and LiUF_5 , KU_2F_9 , $\text{K}_7\text{U}_6\text{F}_{31}$, RbUF_5 , RbU_2F_9 , and $\text{RbF}_3\text{F}_{13}$ (2) oxychlorides: $\text{Cs}_5\text{U}_7\text{O}_{22}\text{Cl}_3$, and AUO_3Cl ($A = \text{Rb}, \text{Cs}$) and (3) oxides: $\text{Cs}_{2.2}\text{U}_5\text{O}_{16}$ and $\text{Cs}_2\text{U}_4\text{O}_{13}$. In addition, we have prepared several new uranium containing silicates and several complex transition metal containing uranates via high temperature flux growth. One significant success was the application of mild hydrothermal routes and, in particular, the

development of the two step approach for synthesizing U(IV) containing fluorides. This approach is general and can be used for the preparation of a wide variety of systems, such as the preparation of V(III) and V(IV) containing oxides. In addition to the successful preparation of uranium containing phases, we also prepared non-uranium containing phases, including vanadates (α - $\text{Na}_5\text{V}_3\text{F}_{14}$, β - $\text{Na}_5\text{V}_3\text{F}_{14}$, $\text{Na}_4\text{V}_2\text{O}_2\text{F}_8$, Pb_2VOF_6 , $\text{Pb}_7\text{V}_4\text{O}_8\text{F}_{18}$, and $\text{Sr}_4\text{V}_3\text{O}_5\text{F}_{13}$), titanates ($\text{PbTiF}_5(\text{H}_2\text{O})$ and K_2TiOF_4), copper salts, $[\text{Cu}(\text{H}_2\text{O})_4]_3[\text{M}(\text{III})\text{F}_6]$ ($\text{M} = \text{V}, \text{Cr}, \text{Mn}, \text{Fe}$) and other fluorides ($\text{PbMn}(\text{III})\text{F}_5\text{H}_2\text{O}$).

DOE National Laboratories

Physical Chemistry of Inorganic Nanostructures

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Funding: \$975,000 (2014)

PROGRAM SCOPE

Advancement in the synthetic control of nanocrystals and nanowires for their use in integrated systems; establishment of core science and technology to produce, separate, and transport charges; and measurement and interpretation of the interactions of nanostructured materials at interfaces, including inorganic-organic, semiconductor-semiconductor, and semiconductor-catalyst interfaces.

FY 2014 HIGHLIGHTS

The research project is a collaborative effort to understand fundamental interfacial charge transfer. We have developed a table-top high harmonic generation spectroscopy setup in the extreme ultraviolet that combines the ultrafast time resolution of optical methods with the electronic structure sensitivity of X-ray techniques to probe detailed carrier dynamics in solid-state semiconductor systems in vacuum and in solvent environments. Pumping with 400 nm light, we detected the ligand to metal charge transfer (LCMT) of Fe_2O_3 (Vura-Weiss *et al.*, *Phys Chem Lett*, 2014). Similar studies were conducted on the Co M-edge of the mixed-valence spinel Co_3O_4 (Jiang *et al.*, *J. Phys. Chem. C*, 2014). We then extended this technique to studying charge dynamics of Co_3O_4 in methanol (Baker *et. al.* *Nano Lett.* 2014). Co_3O_4 decays to ground state in liquid methanol in 600 ps compared to 1.9 ns in vacuum, and the faster dynamics in methanol is associated with hole transfer and recombination at the liquid interface. Other advances include theoretical studies demonstrating that hole transfer from photoexcited quantum dots (QDs) to surface-bound ferrocene occurs in the Marcus inverted region (Tarafer *et al.* *JACS* 2014). Promising new materials and heterostructures have also been made. We used a solid state diffusion method that utilizes atomic layer deposition to controllably alter the composition of rutile TiO_2 nanowires to incorporate Mn dopants, achieving improved electrocatalytic properties for water oxidation (Resasco *et. al.* *JACS* 2014). A synthesized $\text{WO}_3/\text{BiVO}_4$ core/shell nanowire photoanode also achieved the highest product of light absorption and charge separation efficiencies among BiVO_4 -based photoanodes to date (Rae *et. al.* *Nano Lett* 2014). In the next period, we will utilize the developed X-ray techniques to study the fundamental charge dynamics of promising heterostructures and materials.

Two-Dimensional Chalcogenide Nanomaterials

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Funding: \$1,100,000 (2014)

PROGRAM SCOPE

Our long-term vision is to build a cutting-edge research program developing an exciting class of two-dimensional (2D) chalcogenide (O, S, Se, Te) nanomaterials, which can generate high impact on a wide range of DoE BES priorities in materials design and control. Our central focus is understanding and utilizing the modification of the physical properties of these materials by their heterogeneous ionic environment. Here this ionic environment is realized through synthesis of heterostructured interfaces, electric double layer gating, electrochemical intercalation and chemical tuning. Based on the past excellent research accomplishments in this area, the co-PI's (Yi Cui, Harold Hwang, Jun-Sik Lee and Shoucheng Zhang) integrate their research activity synergistically to explore an exciting territory of 2D nanomaterials discovery, computational design, synthesis and novel properties. To reach this long-term vision, this proposal outlines three thrusts of research to be conducted within the next three years:

- Thrust 1. Design and synthesis of novel 2D nanomaterials focusing on interfaces between different ionic environments.
- Thrust 2. Ionic tuning of 2D nanomaterials by electric double layer gating, electrochemical interaction and chemical tuning.
- Thrust 3. Probe and manipulate the exciting electronic and photonic properties of these novel materials.

FY 2014 HIGHLIGHTS

This project was initiated in September 2014. Highlights are forthcoming in fiscal year 2015.

Nanostructured Carbon Films

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Funding: \$946,000 (2014)

PROGRAM SCOPE

In this program we seek a fundamental understanding of a novel class of materials based on supported subnanometer clusters and support materials under electrochemical conditions. We use our unique capabilities to synthesize well-defined small clusters of specific size and composition, which we have demonstrated that on the right type of support they can be stable, highly active, and selective for a variety of catalytic reactions. Materials based on size-specific subnanometer clusters are attractive for catalysis because (1) they have well-defined and identical catalytic sites, (2) the number of sites can be precisely controlled, (3) their activity can provide valuable insights into catalytic mechanisms, and (4) calculations can be done at sufficient accuracy to allow guidance for design of optimal clusters. Two other key parts to this program are the support materials and computational materials design. One of the supports that we are using is a new form of diamond referred to as ultrananocrystalline diamond (UNCD), which has many unique properties due to combining sp^3 diamond grains with sp^2 -like carbon grain boundaries in one material. We also use our capabilities to synthesize metal oxide supports for the clusters. This can open up many more opportunities to tailor the catalytic activity as the choice of support can have dramatic effect on the catalytic properties of subnanometer clusters. Another key part of this program is the use of characterization and computational capabilities to both understand the properties of the new cluster/nanocarbon composites as well as to perform screening to find optimal candidate clusters to be used on the supports.

FY 2014 HIGHLIGHTS

(1) Size selected Ag clusters for understanding Li-O₂ electrochemistry: In this study of the discharge product morphology Li-O₂ electrochemistry based on precisely controlled subnanometer transition metal cluster catalysts added to a carbon cathode has revealed that these small clusters can be sites for oxygen reduction and that nucleation and growth occurs on separate sites on the cathode suggesting a solution phase process is involved during discharge. This study of specific and well-defined size ORR active sites provided evidence for the first time that metal catalysts can be used to control discharge products in Li-O₂ electrochemistry and provides a potential avenue to reduce the charge overpotentials and increase capacities with less reactive surface morphologies. (2) Characterization of size selected Ag clusters: High resolution transmission electron microscopy has been used to image subnanometer Ag clusters for the first time. The images were taken of fifteen atoms clusters on a carbon surface and have revealed their shape as well as provided direct evidence that the clusters do not agglomerate until a high enough coverage on the surface is reached. This study was part of the study of Li-O₂ electrochemistry described in the first bullet. (3) Electrocatalytic CO₂ reduction on metal clusters: Computational studies of electrochemical reduction of CO₂ to CO, HCOOH and CH₄ were carried out using tetra-atomic transition metal clusters (Fe₄, Co₄, Ni₄, Cu₄ and Pt₄). Novel catalytic properties were predicted for these subnanometer clusters, suggesting that they may be good candidate materials for electrocatalytic CO₂ reduction. Experimental studies are planned to confirm the theoretical predictions. (4) Water splitting on iron oxide supports: Subnanometer Co clusters have been investigated as water splitting electrocatalysts and electrophotocatalysts. The studies identified sub-nm Co cluster supported on iron oxide as active in water splitting.

Materials and Interfacial Chemistry for Next Generation Electrical Energy Storage

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Funding: \$582,000 (2014)

The University of Texas at Austin part of this project is listed separately under Principal Investigator: John Goodenough.

PROGRAM SCOPE

Electrical energy storage (EES) in rechargeable lithium-ion batteries is the principal power source for portable electronic devices. As pointed out in the BES Workshop on Electrical Energy Storage, batteries are also needed for effective use of clean, renewable wind and solar energies. This proposal focuses on developing a firm fundamental understanding of the electrode and electrolyte materials and the chemistry at their interfaces that will allow improvement of existing battery strategies as well as the development of alternative battery strategies to meet these challenges. To address the design of improved solid electrodes, the choice of active micro- or nano-particles and their low-cost incorporation into composites with optimal architectures of conductive materials, e.g. polymers, graphene sheets, or amorphous carbon, need to be rationalized. Moreover, the solid-electrode interface with the electrolyte needs to be optimized for Li^+ or Na^+ transfer across it, which includes surface modifications as well as understanding the formation chemistries of any passivating solid-electrolyte interphase (SEI) layer. The latter task requires *in situ* characterizations of surface structures and interface chemistries. To develop alternative battery strategies that allow the use of lithium or sodium anodes and air or liquid-flow-through cathodes, the design and characterization of solid and/or composite solid/polymer-gel Li^+ and/or Na^+ electrolytes as mechanically robust membrane separators need to be undertaken. Membrane design must include investigation of oxide-polymer interactions and barriers to Li^+ / Na^+ transfer across oxide-polymer interfaces. To address these fundamental issues, this project brings together an integrated effort between the University of Texas at Austin (UT Austin) and the Oak Ridge National Laboratory (ORNL), involving strong solid-state and polymer science coupled with advanced characterization and synthetic techniques at the two institutions.

FY 2014 HIGHLIGHTS

(a) A new orthochelated salt, lithium bis(monofluoromalonato)borate (LiBFMB), is synthesized and purified. The presence of fluorine in borate anion of LiBFMB increases its oxidation potential and also facilitates ion dissociation. (b) A TiNb_2O_7 nanoporous anode material was prepared by a facile approach. The interconnected nanoporous framework composed of nanocrystals leads to enhanced rate and cycling performance with high coulombic efficiency. (c) The synthesis of mesoporous Prussian blue analogues through a template-free methodology and the application of these mesoporous materials as high-performance cathode materials in sodium-ion batteries were demonstrated. Crystalline mesostructures were produced through a synergistically coupled nanocrystal formation and aggregation mechanism. (d) A unique class of air-stable magnesium electrolytes was developed based on alkoxide magnesium compounds. The crystals obtained from this class of electrolytes exhibit a unique structure of tri-magnesium cluster, $[\text{Mg}_3\text{Cl}_3(\text{OR})_2(\text{THF})_6] [(\text{THF})\text{MgCl}_3]$. (e) A novel ambient Li-SO_2 battery was developed through the introduction of ionic liquid electrolyte with tailored basicities to capture SO_2 via reversible chemical absorption. (f) The phase changes accompanying the second Li^+ insertion into alpha-

LiVOPO_4 and $\beta\text{-LiVOPO}_4$ are presented at various degrees of lithiation, employing both electrochemical and chemical lithiation. The accompanying structural changes are evidenced by X-ray and neutron powder diffraction. (g) The interfacial structure of a Si battery electrode was determined *in situ* using neutron reflectometry. These measurements show the formation of a reaction layer before lithiation. (h) The intrinsic reaction chemistry of Na with a variety of metal anode materials was investigated. This data showed that Na would only diffuse 3 nm within the Cu_6Sn_5 electrode material. This result enabled us to predict particle sizes which would lead to optimal Na storage properties.

Fundamental Charge Transfer Processes in Stable Free-Radical Organic Polymer Systems

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Funding: \$381,000 (2014)

PROGRAM SCOPE

Polymers with stable pendant radical groups are an emerging class of redox-active materials with potential application within the next generation of hybrid energy storage matrices. These polymeric materials have demonstrated a unique set of remarkably rapid, efficient and reversible charge-transfer processes. However, there is currently not an advanced understanding of the mechanism(s) involved in electron and/or ion transfer for these polymeric materials. This lack of understanding hinders rational design efforts to improve the electroactive properties of radical containing polymers. The focus of this project is to advance the fundamental understanding of the structure-property relationships associated with the mechanism(s) of electron transfer and ion transport, along with the associated interfacial electron- and mass-transfer processes that impact the charge-transfer processes of this class of organic free-radical polymeric redox active materials. Through an integrated research approach that combines chemical synthesis, electrochemistry, spectroscopy and theoretical modeling applied to a series of stable organic radical materials, we have focused our efforts to establish how the morphologies of the polymer films impact the physio-chemical properties of the organic-based radical materials. Subsequently, the directed syntheses of new materials with tailored properties are utilized to test our models and further advance the understanding of charge transfer in both solution phase and solid-state organic redox systems. This work has crosscutting implications within energy applications such as battery systems, organic-based photovoltaic materials, the use of organic membranes in fuel cells, and more broadly in the use of polymeric materials for organic electronics.

FY 2014 HIGHLIGHTS

In FY 2014, we focused on the 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO) organic radical moiety incorporated into a complex materials set of poly(4-methacryloyloxy-2,2,6,6-tetramethylpiperidine-N-oxyl) (PTMA) to probe, and establish, the charge-transfer mechanisms for a series of the TEMPO-containing macromolecules with varying radical fractions, chain lengths and side-chain compositions. Our research indicated that the majority of radicals participate in similar intra- and inter-molecular radical-radical interactions regardless of TEMPO moiety fraction and/or solid versus solvated state. It is these stable radical-radical interactions that control molecular packing and are responsible for the rapid self-exchange charge transfer and electron-transfer reactions observed electrochemically. Through

atomistic molecular dynamics simulations of the structure and morphology of polymer films we were able to establish that inter-TEMPO separations are controlled by steric repulsions between methyl groups that dictate the inter- and intra- molecular packing within the various PTMA materials. Electron spin resonance (CW X-band) evaluation of the radical-polymer local environment in both liquid and solid state indicates that the majority of radicals participate in multiple interactions, regardless of TEMPO moiety fraction. Furthermore the approximate radical-radical distances, $\sim 5 \text{ \AA}$, correlates well with our theoretical predictions that show an effective electron transfer length of 5.5 \AA , with a majority of the electron transfer, nearly 85%, occurring between radical sites on different polymer chains in the solid state. In solution, theory predicts the same local environment for the radical-radical separations, although the interactions were intra-molecular rather than inter-molecular. Finally, to investigate the rate of charge transfer during oxidation we exploited the fluorescence quenching properties of the nitroxide radical.

Giant Nanocrystal Quantum Dots

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Funding: \$631,000 (2014)

PROGRAM SCOPE

Science challenges remain as underpinning drivers of fundamental research required for disruptive advances in solid state lighting (SSL). A fundamental understanding of the processes that impact the conversion of electricity into light is still needed. Nanostructures can serve as platforms for understanding such fundamental processes, but also as solutions to realizing control over exciton \rightarrow photon conversion pathways. In the past year, remarkable progress has been made in the commercial introduction of colloidal nanocrystal quantum dots (NQDs) as unique down-conversion phosphors in small and large display technologies. However, despite this clear advance, applying NQDs to SSL remains challenged by the more rigorous demands of lighting platforms compared to displays, where, e.g., high photon flux and high temperatures must be simultaneously tolerated. In our work, we study and develop a new class of optical nanomaterial – the “giant” NQD (g-NQD) – and its structural variations. g-NQDs exhibit unique properties (non-blinking, non-photobleaching, suppressed Auger recombination, large Stokes shift, surface-independent emission) ideal for SSL. Through three Research Goals, we aim to establish g-NQDs as optimally functional “building blocks” for lighting, with an unprecedented combination of stability/ solid-state performance, high efficiency, low-cost and color tunability: (1) Establish design principles for existing and new g-NQDs (non-rare, non-toxic): (a) Determine process-structure-function correlations and (b) Exploit quasi-combinatorial synthesis aided by *in situ* diagnostics, (2) Understand exciton and multiexciton \rightarrow photon conversion pathways as realized through: (a) Designed manipulation of intrinsic nanoscale heterostructures and (b) Extrinsic field control, especially plasmonic manipulation of recombination processes, and (3) Develop and validate g-NQD device constructs informed by (1) & (2).

FY 2014 HIGHLIGHTS

(1) New 'plasmonic g-NQDs' elucidated/demonstrated: Novel hybrid nano-structures show that we can combine ultrastability of g-NQD quantum emitters with plasmonic field effects provided by an external gold shell, including manipulation of emitter decay processes. (2) Employing project-developed "design principles" for optimal exciton-to-photon conversion: (a) Completed studies of new g-NQDs based on ZnSe/CdS and CdSe/ZnSe, where syntheses complicated by instability against cation exchange and alloying during growth, respectively. Systems used to validate impact of electronic structure on g-NQD properties. (b) Optimized new InP/CdSe/CdS g-NQDs for first dual non-blinking photoluminescence in the visible and near-IR regimes. (3) "Extrinsic-control" studies: Shell-thickness-dependent single-dot spectroscopy investigation of NQD/ graphene couples completed; showed enhanced biexciton quantum yields (BE-QYs) at thick shells with implications for novel lasing devices and entangled-photon generation. We further revealed that collective oscillations of local excess electron/hole density formed at the g-NQD/graphene interface yield a novel "plasmon mode," with important implications for extending graphene plasmonics to visible/near-IR regime and new plasmonic cavity/waveguide design approaches. (4) Facilitating extrinsic control via precision nanoscale integration: (a) Developed two-step e-beam lithography to place single g-NQDs at center of gap-bar nano-antennas; revealed plasmon-assisted energy transfer and plasmonic field's influence on multi-exciton Auger recombination. (b) Optimized dip-pen nanolithography approach for precisely placing <10 NQDs onto sub-micron 3-D structures?

Rational Synthesis of Superconductors

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Funding: \$631,000 (2014)

PROGRAM SCOPE

This project is a material synthesis program using a multi-faceted approach that combines the rational design of novel materials with structural and electronic characterization probes. We hypothesize that the conception of homologous series of phases with tunable building blocks enables the generation of specific and desirable compositions with predictable structures. This strategy is coherent and can yield novel compounds with specific characteristics desirable for achieving the goals of this program. We focus on materials with a high degree of structural and compositional freedom and chemical/electronic complexity with which to investigate (a) density-wave instabilities (spin and charge), and their suppression through chemical doping in order to generate superconductivity that may emerge from phase competition, and (b) how narrow energy band gaps and facile doping properties could lead to a superconducting state. In the former we investigate low-dimensional intermetallics exhibiting magnetic interactions and spin density waves. In the latter we investigate narrow band ternary and quaternary chalcogenide phases comprising heavy elements such as lead, bismuth, selenium and tellurium. We use a conceptually robust tool in designing, predicting and creating sequences of structurally related materials. The project focuses on relationships between structure, composition, electronic structure and physical properties. In the long term, we expect to clarify the influence of various building blocks on the physical properties and enhance our ability to further design members exhibiting superconductivity.

FY 2014 HIGHLIGHTS

Experimental procedures for synthesis and crystal growth were optimally refined to generate high quality polycrystalline and single crystals of $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ and $\text{Ba}_{1-x}\text{Na}_x\text{Fe}_2\text{As}_2$ across the entire phase diagram. The results also enabled us for the first time to observe re-entrant magnetic order coincident with superconductivity at low temperatures in the $\text{Ba}_{1-x}\text{Na}_x\text{Fe}_2\text{As}_2$ series. For a very narrow Na composition range ($0.24 \leq x \leq 0.28$), the orthorhombic superconducting phase is accompanied by a re-entrant tetragonal antiferromagnetic phase. This finding is a crucial step toward the understanding of the mechanism of superconductivity in the iron pnictides (and perhaps by extension, all high-temperature superconductors in general). $\text{LaPd}_{1-x}\text{Bi}_2$ featuring Bi-square nets and PbO-type PdBi layers was also studied. By creating Pd vacancies the Fermi surface nesting is avoided which suppresses any potential charge density wave (CDW) on the Bi net, apparently allowing the emergence of bulk superconductivity. A strong scattering effect presumably induced by Pd vacancies suggests an s-wave pairing symmetry in $\text{LaPd}_{1-x}\text{Bi}_2$. Hall effect measurements reveal dominantly electron-like charge carriers and single-band transport behavior and the magnetization and broadening of the resistivity transition was measured under different magnetic fields demonstrating a high upper critical field of 3 T. The $\text{CePd}_{1-x}\text{Bi}_2$ analog is non-superconducting but shows antiferromagnetic order below 6 K. On the opposite side of the property spectrum are semiconductors which do not exhibit spin density wave states and historically have not been a source of superconductor materials. Recent results, however, are helping to change this view and promise to open up vast new phase space for investigations. The narrow band gap semiconductor CsBi_4Te_6 were doped to become a new superconductor with T_c around 4 K. Also, noticeable in this CsBi_4Te_6 superconductor is an exceptionally high upper critical field (H_{c2}) up to 10 T observed.

Energy and Fuels from Multifunctional Electrochemical Interfaces

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Funding: \$1,125,000 (2014)

PROGRAM SCOPE

We propose an interdisciplinary, atomic/molecular level approach, integrating both experimental- and computational-based methodologies to design, synthesize, and characterize electrochemical (EC) interfaces with tailored properties, with a specific focus on addressing closed-loop energy/chemical/environmental cycles based on water, carbon, and lithium. Two fold strategies will be used: (i) first is based on a materials-by-design strategy, involving transferring the knowledge gained from the single crystalline materials and thin metal films to nanoscale materials; and (ii) the second relies on the double-layer-by-design strategy, bearing precise organization of multiple functionalities of the electrolyte components at the sub-nano-scale regime that is operating in the double layer. These two strategies form a closed-loop material/electrolyte design approach wherein the knowledge gained from the model systems is used to tailor the more complex, real-world systems. The range of materials and electrolytes that will be explored by these two strategies is broad, involving metals, metal/metal-oxides, pure oxides, sulfur-based and carbon-based materials as well as aqueous electrolytes with a

wide pH range and organic solvents that are traditionally used in the battery systems. The methods for unraveling complexities that is controlling interfacial properties is diverse, ranging from *ex situ* and *in situ* optical methods to microscopy-based structural probes to synchrotron-based techniques and classical electrochemical methods. Advancing in fundamental understanding of the reaction mechanisms and kinetics involved on well-characterized metal, oxide, and metal/metal-oxide materials in both aqueous-based and organic-based environments will be critical in our quest to learn how to design efficient, stable and selective electrochemical systems that are needed by our society.

FY 2014 HIGHLIGHTS

- Established functional links between conductivity, stability and activity of SrRuO₃ single crystal thin metal films in the oxygen evolution reaction.
- Designed new generation of active and stable Ru-Ir based catalysts for the water splitting reaction and oxygen production in acidic-based electrolyzers.
- Based on electrocatalytic trends for the hydrogen oxidation reaction in alkaline solutions, developed cost-effective catalysts with the highest activity ever observed in alkaline environments (two orders of magnitude more active than the state-of-the-art Pt-based materials).
- Established new guiding principles for the development of bi-functional catalysts for efficient transformation of hydrogen energy into electricity in fuel cells and electrolyzers.
- Based on fundamental knowledge established on single crystal surfaces, designed mesostructured thin films catalysts, with adjustable structure and composition, for the oxygen reduction reaction in PEM based fuel cells.
- Developed surface science approach for studying electrochemical interfaces in organic solvents.

Diamondoid Science and Applications

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Funding: \$768,000 (2014)

PROGRAM SCOPE

This program explores the synthetic, electronic, and self-assembly aspects of diamondoids, a new class of hydrogen-terminated molecular diamonds. These materials bridges the gap between small molecules and nanoparticles, having some of the benefits of small molecule chemistry, such as atomically defined structures, site selective functionalization, and facile organization, and some of the benefits of nanoparticles, such as excellent electronic properties, robustness, and strong interaction forces. These materials have demonstrated an amazing ability to regulate the energy of electrons flowing through single monolayer films, form 'extreme' carbon-carbon bonding structures, and dramatically enhanced electron emission processes. We study these systems through a set of interrelated synthetic modifications, self-assembly, X-ray scattering, templating, and electron transfer studies. We seek to understand how the unique combination of the rigid lattice and sp³ hybridization lead to the unique properties compared to related alkane or sp²-based carbon systems.

FY 2014 HIGHLIGHTS

(1) Developing new methods for selective C-C bond modification. Diamondoids are an ideal system to explore the limits of synthetic control due to the remarkably similar molecular reaction sites, requiring subtle manipulation of chemical reactivity for site-selective modifications. We have developed several significant modification schemes to provide broad functionality to the diamondoids. In particular, vinyl adducts are a well known functional group that can incorporate diamondoids into a wide variety of systems, ranging from diamondoid based polymers to surface modifications (2) Diamondoid-C₆₀ molecular rectifiers. We reported a novel all-hydrocarbon molecular rectifier consisting of a diamantane-C₆₀ conjugate. By linking both sp³ (diamondoid) and sp² (fullerene) carbon allotropes, this hybrid molecule opposingly pairs negative and positive electron affinity moieties. The morphology and single-molecule conductances of self-assembled diamantane-C₆₀ domains on Au(111), probed by low-temperature scanning tunneling microscopy and spectroscopy, reveal a large rectifying response of the molecular constructs. This specific electronic behavior is postulated to originate from the electrostatic repulsion of diamantane-C₆₀ molecules due to positively-charged terminal hydrogen atoms on the diamondoid interacting with the top electrode (scanning tip) at various bias voltages.

Innovative and Complex Metal-Rich Materials

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Funding: \$737,000 (2014)

PROGRAM SCOPE

This project strives (i) to uncover and ultimately design new families of intermetallic phases; (ii) to understand the factors that stabilize both new and known metal-rich phases by combining exploratory synthesis and temperature-dependent structure determinations with electronic structure theory; and (iii) to establish structure-property relationships for complex metal-rich materials as related to both practical as well as fundamental issues, e.g., thermoelectric, magnetocaloric, catalytic, and magnetic behavior. Targeted compound classes include, but are not limited to, Hume-Rothery types, polar intermetallics, quasicrystalline and approximant phases, and complex metallic alloys of transition metals. Significant focus includes (i) compounds involving reduced environments for elements of the late 5th and 6th period transition elements (Pd, Pt, Ag, Au), which offer filled d-bands and relativistic enhancements of chemical bonding; (ii) Li-rich intermetallics, taking advantage of Li's dual role of both an active as well as an electronegative metal in chemically reduced environments; and (iii) 3d metal systems grown in reactive and eutectic fluxes.

FY 2014 HIGHLIGHTS

Discovery of new compounds with unusual metal-metal bonds and thorough studies of certain phase spaces were accomplished during the past year. Achievements include the discovery all three ordered BaAl₄-type variants in the Ba-Au-Sn system, which allows, for the first time, the development of a unified view on the interplay between valence electron counts and phase stabilities of these three prolific,

ordered derivatives of the $BaAl_4$ -type. Following up on the lessons learned, a systematic study of the Sr-Au-Sn system was accomplished. Toward a search for new anode materials, we discovered three new Ca-Li-Zn compounds. The understanding of Li-induced Zn clustering in these phases may help to understand the formation of Zn dendrites on electrodes during charge-discharge cycles for Zn batteries. Interpretation of these structures challenges the current Zintl-Klemm concepts of chemical bonding in polar intermetallics. We discovered and characterized new reduced gold and platinum metal-rich compounds with unusual bonding modes and noncollinear magnetic ordering, demonstrating how electronegative gold atoms can serve as ligands (“pseudo-halides”) to transition metals like manganese and provide exchange pathways between magnetically-active 3d metals with rare earth metals. Moreover, new bonding motifs involving the electronegative metals are broadening our understanding of metal-metal bonding within intermetallics. Additionally, the team discovered new ferromagnetic gamma-brasses, re-examined the compositions, structures, and atomic distributions in Fe-Zn and Co-Zn gamma brasses, and discovered two large unit cell structures built of icosahedra using a Zn/Sn flux with 3d transition metals like chromium and vanadium. In collaboration with other groups, we discovered various new phases and a new ferromagnetic Mn-doped (5-15 at.%) rhombohedral-boron with Curie temperature of 500 K and a magnetic moment of $2.4 \mu_B/\text{Mn}$ at 300 K.

Nuclear Magnetic Resonance

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Funding: \$970,000 (2014)

PROGRAM SCOPE

With the support of the DOE BES, our group develops new methods and technologies based on nuclear magnetic resonance and magnetic resonance imaging for the non-invasive investigation of materials structure, function, chemistry, and organization at all length scales. We seek to decrease the dependence of magnetic resonance on expensive infrastructure and lengthy experiments and to enable new applications with enhanced portability and sensitivity. We collaborate with other MSD core programs both to develop new materials and structures used in our own experiments and to pursue exemplary applications of the technology we develop.

FY 2014 HIGHLIGHTS

We harnessed nitrogen vacancy (NV-) centers in diamond as a means of detecting nearby spins. By monitoring the fluorescence of these defect centers, we are able to probe their spin state and extract information about their environment. This enabled the development of “cross relaxation spectroscopy” where spectroscopic information of surrounding electron spins is obtained. We identified long-lived nuclear spin states at zero magnetic field, which take advantage of the inherent symmetry of the zero-field environment to protect the nuclear spin state from a fluctuating environment. These states may be used, in conjunction with nuclear hyperpolarization techniques, to store nuclear spin order for extended time periods. We made significant progress towards miniaturization of xenon-based NMR systems with the development of on-chip xenon hyperpolarization, encoding and detection. This advance opens up the possibility for sensitive, portable sensors that bring NMR outside of the lab and into new fields. Our

work continues on improving the fundamental sensitivity of xenon-based NMR on multiple fronts including: shift enhancement via paramagnetic sensors; microfluidic-based assays with remote detection, and relaxation based sensors that work in the absence of strong magnetic fields.

Hydroxide Conductors for Energy Conversion Devices

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Funding: \$288,000 (2014)

PROGRAM SCOPE

Stable, hydroxide conducting anion exchange membranes can act as enabling elements of several energy conversion and storage technologies. The primary goal of this project is to understand and improve the hydroxide stability of covalently tetherable cations for their incorporation into anion exchange membranes. We have investigated hydroxide stability of cations using a combined computational and experimental approach. Our work initially focused on ammonium based cations that have been the standard materials employed in anion exchange membranes. We have used computational modeling to validate experimental results and to lead our efforts to develop more robust cations. We have investigated the impact of chemical substitution on the stability of cations. BTMA is the cation that has been the most studied for polymer incorporation and currently dominates anion exchange media. For practical purposes, BTMA is small, compact, relatively basic, and cheap/easy to synthesis, so if it was displaced from this application it would have to be due to other factors. Our most recent efforts have focused on cation chemistries of imidazolium, phosphonium, and (substituted) benzyl trimethyl ammonium (BTMA). Results have shown that imidazolium and phosphonium moieties exhibit large changes in degradation energy barriers while BTMA shows relatively small changes. Our experimental studies have focused on coordination with our computational studies, as well as method development for more reproducible and reliable measurements of durability. BTMA has been used as a model molecule and its durability (in the first comprehensive and reproducible studies presented in the literature) was found to be significantly more durable than previously reported. This increase in durability was determined by isolating specific accelerants that were common in the experimentally difficult approach for studying high temperature, high pH degradation.

FY 2014 HIGHLIGHTS

FY 2014 resulted in detailed studies of degradation reactions of benzyl trimethylammonium (BTMA). Through literature review and experience with hydroxide based degradation studies, we had noticed a trend of inconsistent experimental findings for reported degradation rates of cations. Unfortunately, performing repeatable and accurate measurements under high pH, high temperature conditions is exceptionally challenging. We have developed advanced degradation techniques involving hermetically sealed Teflon reactors, known thermal responses, avoided the use of deuterium, and determined acceptable (low) concentration of cations that avoid phase separation. Through these studies we have accurately quantified the degradation rate of BTMA and shown that BTMA is much more stable than previously assumed with approximately 10% degradation over 5000 hours at 80C. Conditions which suggest its ability to be used in specific applications may already be acceptable. We also looked at the

influence of systematic substitution to impact the stability of BTMA. Computationally we investigated methyl, methoxy, nitro, hydroxyl, primary amine and complex amine substitution (both single substitutions and multiple substitutions). Experimentally we have investigated methoxy and nitro substitutions. We have found that modest gains can be realized by specific substitution groups and patterns, but these stability improvements result in less than an order of magnitude increase in stability, which is far less than what we have observed for either imidazolium based cations or phosphonium based cations (two advanced cation families that we have also investigated). We have significantly increased our interactions with other research groups who have begun to recognize our specific methods and tools as novel and advanced including Dan Knauss (Colorado School of Mines), Yusan Yan (Delaware), Mike Hickner (Penn State), and Chulsung Bae (RPI).

Chemical and Mechanical Properties of Surfaces, Interfaces and Nanostructures

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Funding: \$1,601,000 (2014)

PROGRAM SCOPE

In this program we carry out atomic and molecular level studies of surfaces and interfaces, focusing on structure, adsorption, reactions, energy transfer across interfaces, and nanoparticle growth, to obtain a fundamental understanding of the mechanisms that govern the physical, chemical, catalytic and tribological properties of materials. We study how the structure of surfaces determines these properties, and how energy is transferred by vibrational, electronic and photonic excitations of surface atoms and molecules. Single crystals and nanoparticles are key materials investigated. An important activity is the development of techniques and methods that make possible surface sensitive microscopy and spectroscopy studies of surfaces in different environments, expanding the ultrahigh vacuum environment of traditional surface science to ambient gas pressures and to solid-liquid interfaces. The basic science of the solid-liquid interface is a new frontier that has been opened by the recent development of new instruments and techniques. It is a central piece of our strategy for the future that we plan to develop.

FY 2014 HIGHLIGHTS

Atoms at step edges are the most reactive and are active in catalyzing many reactions. The critical influence of their geometric arrangement on Pt(111) surfaces towards their reactivity under ethylene and CO was revealed using Scanning Tunneling Microscopy *in situ*. While CO molecules reconstruct the steps at pressures of 1 Torr, causing the formation of clusters of atoms, ethylene can reverse this reconstruction. This occurs only on steps with atoms arranged in triangular motifs. Ethylene can't restore the initial steps when atoms are arranged in square motifs, due to the fact that ethynylidyne, the adsorption product of ethylene, adsorbs only on triangular motifs of atoms. This shows that even small changes in atomic geometry of the catalyst atoms leads to important changes in reactivity. We synthesized highly active and durable electrocatalysts by exploiting the structural evolution of platinum-nickel (Pt-Ni) bimetallic nanocrystals. The starting material, crystalline PtNi₃, transforms in solution by

interior erosion of Ni atoms into Pt₃Ni nanoframes, with three-dimensional molecular accessibility. Both interior and exterior catalytic surfaces of this open-framework structure are composed of a segregated Pt-skin structure exhibiting enhanced oxygen reduction reaction activity. The Pt₃Ni nanoframe catalysts achieved a factor of 36 enhancement in mass activity and a factor of 22 enhancement in specific activity during prolonged exposure to reaction conditions. The structure of H₂O in the double layer on biased gold electrodes was determined for the first time with a combination of x-ray absorption spectroscopy and first principles calculations. At zero or positive bias, about 50% of the molecules lie flat on the surface with all H bonds saturated, and 30% with broken H bonds that do not contribute to the x-ray spectrum. At negative bias, the population of flat-lying molecules with broken H bonds increases, producing a spectrum similar to that of bulk H₂O.

Directed Energy Interactions with Surfaces

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Funding: \$504,000 (2014)

PROGRAM SCOPE

The Directed Energy Interactions with Surfaces program focuses on fundamental studies of the interaction of directed energy sources such as energetic ions with materials, which provides the basis for characterizing and modifying materials. Fundamental understanding of energy-material interactions drives the development of world-class instruments and methods for materials characterization, which in turn enables us to answer questions about new or previously unobservable phenomena and develop new materials. The long-term goal is to understand the interaction of directed energy sources with materials, both in model systems in which basic interactions can be studied in great detail, and in complex systems relevant to DOE missions in which multiple interactions occur and evolve over varying length and time scales.

FY 2014 HIGHLIGHTS

Ion sputtering as a means of generating clusters of various compositions remains one of the least understood phenomena in particle-solid interactions. During sputtering, three distinct processes, i.e. cluster formation, ionization, and fragmentation, occur quasi-simultaneously; the challenge is to distinguish between them and learn basic laws driving the cluster formation process. Secondary Neutral Mass Spectrometry (SNMS) with Single Photon Ionization (SPI) minimizes fragmentation while separating cluster formation and ionization. Recently we applied SMNS-SPI to cluster emission from the ternary alloy Au₇Cu₅Al₄, with a focus on the effect of surface modification via ion irradiation. The cluster yield after pretreatment with Ar⁺ ions shows a large energy-dependent change. High-energy pretreatment significantly enhances Al-containing clusters, while low-energy pretreatment significantly enhances Au-containing clusters. We have previously shown that the cluster yield depends strongly on the first layer composition of the alloy. Preferential sputtering is well known and could account for changes in the relative cluster yields for low ion doses, but this is not the case here. Furthermore, the effect persists for large clusters, which are relatively insensitive to the surface composition. The Ar⁺

penetration depth decreases with ion energy, with a maximum in the first 2-5 monolayers. XPS measurements indicate that some Ar is implanted, though amounts are not expected to remain at such shallow depths. This must be quantified since implanted Ar atoms near the surface would have an effect on sputtering yields. Cluster compositions and yields are clearly affected by chemical and morphological changes due to irradiation, and represent a sensitive measure of the surface state, one that gives different and perhaps richer information than simply surface concentration.

Materials Chemistry - Solid State NMR

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Funding: \$703,000 (2014)

PROGRAM SCOPE

It is the purpose of this program to develop and apply advanced solid-state nuclear magnetic resonance (NMR) techniques for elucidating the structure and dynamics of complex organic, nanocomposite, and semiconductor materials with interesting properties. Modern multinuclear NMR can provide detailed information on the composition and supramolecular structure of complex materials, even in the presence of disorder, and guide the rational design of novel materials. The research in this FWP can be grouped into the following focus areas: (1) Nanocomposites, in particular biological (e.g., bone) and related bioinspired materials, by ^{31}P , ^1H , and ^{13}C NMR. (2) Polysaccharide-rich plant cell walls, elucidating how the energy-rich cellulose and hemicellulose are bound to other biopolymers in the cell wall, using 2D and 3D ^{13}C NMR. (3) Proton conductors, such as the Nafion fuel-cell membrane, by ^{19}F and ^{13}C NMR. (4) Thermoelectric tellurides, characterizing by ^{125}Te NMR the distribution of dopants, charge-carrier concentrations, and local symmetry, and correlate with electronic and thermal transport properties measured in-house. (5) NMR of carbon materials as used in supercapacitor electrodes, and nanodiamond, by ^{13}C NMR. (6) General NMR pulse-sequence development to provide new structural information. (7) Simulations of NMR parameters and scattering curves for extracting the maximum information content from the available data.

FY 2014 HIGHLIGHTS

We discovered an unusual inverse relation between the Seebeck coefficient and carrier concentration in $\text{Ag}_x\text{Sb}_x\text{Ge}_{50-2x}\text{Te}_{50}$ materials, which can be explained by strong energy filtering of charge carriers. We demonstrated that ^{125}Te NMR can be used for determination of carrier concentration in multiphase materials, which is not possible to obtain from Hall effect measurements. This year we also showed the effect of replacement of Ge in GeTe by Ag, Sb, and Dy on ^{125}Te NMR spectra, carrier concentration obtained from spin-lattice relaxation and thermoelectric properties measurements. Using dynamic nuclear polarization enhanced solid-state NMR, the Hong group discovered the long-elusive carbohydrate-binding target of the glycoprotein, expansin, in the plant cell wall. Expansin binds hemicellulose-enriched regions of cellulose to loosen the cell wall for growth.

Polymer-Based Multicomponent Materials

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Funding: \$1,925,000 (2014)

PROGRAM SCOPE

Multicomponent polymeric materials are widely used in various modern technologies and will have even broader applications in future technologies, from lightweight materials, to solar cells and electrical energy storage to biomedical technologies. Yet, our fundamental understanding of the processes and interactions that control macroscopic properties in these materials remains limited. The overarching goal of the research proposed herein is to develop a fundamental understanding of how interfacial properties and interactions affect structure, morphology, dynamics, and macroscopic properties of multicomponent polymeric systems. The proposed research focuses on two research themes. The first seeks to correlate properties of polymer-nanoparticle mixtures to the nanoparticle structure and interfacial interactions, while the second involves the correlation of molecular architecture, electrostatic interactions and external fields to the morphology of multiblock copolymer materials. To fully understand the underlying processes and mechanisms, we pursue a comprehensive interdisciplinary approach lead by advanced theory and simulations, precise synthesis with nano-scale control and state-of-the-art characterization (with special emphasis on neutron scattering). The fundamental knowledge developed in this program will contribute to the scientific foundation for the rational design of multicomponent polymer based materials with superior properties and function that can address many DOE challenges such as organic photovoltaics, electrical energy storage and fuel cell membranes, and stronger light-weight materials that result in energy savings.

FY 2014 HIGHLIGHTS

By combining theory, computations and experiment we elucidated the physical mechanisms that determine effective nanoparticle interactions controlling dispersion in polymer nanocomposites (PNC). A theoretical basis has been developed for designing random copolymers to optimize fullerene miscibility. The developed approach predicts a remarkably rich phase behavior and can help guide the development of PNC for photovoltaic applications. The first predictive statistical mechanical theory for activated relaxation in thermal liquids has been formulated. The theory captures the key features of the alpha-relaxation time as a function of temperature and pressure from picoseconds to hundreds of seconds. The approach has been extended to polymers and the role of chain length and stiffness on T_g and fragility elucidated. This advance sets the stage for addressing how confinement and surface/interface effects modify the alpha-relaxation and elasticity in PNCs. Synthesis of soft polystyrene nanoparticles with the size ~ 10 nm has been developed. SANS identified three distinct nanoparticles morphologies that can be well controlled by varying the crosslinking density: (i) fuzzy soft gels; (ii) smooth soft gels; and (iii) dendritic glassy gels. Combining dielectric spectroscopy (DS), DSC and SAXS,

we unraveled the role of nanoparticles on the structure and dynamics of PNC. A thin interfacial polymer layer that has very different density and dynamics than the bulk polymer was deduced. The thickness of the interfacial layer of P₂VP on SiO₂ nanoparticles is ~5 nm in both static (SAXS) and dynamic (DS and DSC) measurements. The layer is not “dead” or “glassy”, but its dynamics are slowed by ~100 times relative to the bulk polymer. These results explain many controversies in the PNC field, provided new insight into the structurally and dynamically heterogeneous nature of PNCs, and demonstrated the need to explicitly consider the interfacial layer to construct predictive models.

Inorganic/Organic Nanocomposites

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Funding: \$1,215,000 (2014)

PROGRAM SCOPE

The Inorganic/Organic Nanocomposite program aims to design and synthesize organic and inorganic building blocks, and guide their assemblies into functional nanocomposite materials by developing a thorough understanding of interfacial electronic properties with an ultimate goal to generate functional hybrid materials with tailored electrical and optical properties.

FY 2014 HIGHLIGHTS

We systematically (1) investigated the phase behavior of supramolecular nanocomposites in thin films to achieve structural control over nanocomposites containing spherical particles and nanorods as well as particle mixtures; (2) performed detailed analysis of assembly process and kinetic pathway that led to optimized solvent annealing process to obtain hierarchically structured nanocomposites in one minute; (3) developed molecular level understanding of surface of PbS nanoparticle both theoretically and experimentally; (4) designed organic conductive ligand to achieve energy level alignment for efficient carrier transport in thin films of nanoparticle solids; and (4) correlated Kelvin probe force microscopy (KPFM) microscopy & spectroscopy with scanning tunneling microscopy/spectroscopy (STM/STS) to study the impurity conduction mechanisms of PbS quantum dots. In addition, we established a new direction to use tetrapod nanocrystals as fluorescent stress probes to investigate the mechanical properties of nanocomposites at nanoscale.

Mechanical Behavior and Radiation Effects

Institutions Receiving Grants

Software Center for Predictive Theory and Modeling

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Students: 4 Postdoctoral Fellow(s), 12 Graduate(s), 0 Undergraduate(s)
Funding: \$2,000,000 (2014)

PROGRAM SCOPE

The overarching goal is to establish a unique scientific platform that will enable accelerated predictive materials science. This will be accomplished by completing the following objectives: 1. Develop and establish PRISMS (PRedictive Integrated Structural Materials Science), a suite of integrated multi-scale computational tools for predicting the microstructural evolution and mechanical behavior of structural metals. This software suite will be open-source extensible, user friendly and efficient. 2. Develop advanced, open source computational methods for metallic materials. 3. Tightly couple the computational methods with advanced experimental methods for determining model inputs, filling gaps in theory and for validation. 4. Demonstrate this integrated capability by making major advances in the quantitative and predictive understanding of magnesium alloys, in particular the phenomena of: (i) complex, microstructure-dependent deformation processes of magnesium alloys; (ii) fatigue, ductility, and stress-strain response of structural metals; (iii) theory of microstructure evolution and its effect on fatigue and ductility. 5. Develop and deploy "The Materials Commons," a knowledge repository and virtual collaboration space for curating, archiving and disseminating information from experiments and computations as well as providing a collaborative platform for development of open-source code with active involvement of a broader PRISMS open source community. The center will establish systematic protocols for extension of this integrated multi-scale computational capability to the development of predictive capabilities for other structural materials and to incorporate emerging modeling and experimental methods.

FY 2014 HIGHLIGHTS

To ensure effective integration of PRISMS Center activities, our science objectives are organized around 'use cases'. These use cases provide a means to establish collaborative communities, advance science

and demonstrate linkages and capabilities. The primary use cases are prediction of precipitate evolution, recrystallization and grain growth, tensile properties and cyclic/fatigue properties of Mg and Mg alloys. Highlights of our technical progress include: • Using the advanced PRISMS statistical mechanics software (CASM), a free energy description was developed for ordering precipitation within hcp Mg-rare earth alloys and structural transitions from ordered hcp to ordered bcc. • Used the massively parallel PRISMS phase field code with the CASM-determined energetics to predict growth of β' precipitates in Mg-Nd alloys. • Through high resolution imaging and quantification of chemistry and morphology of precipitates, identified key phenomena in the sequence of phase transformations. • Completed real space DFT calculations that estimated that core-size of edge dislocation in aluminum are three times larger than indicated by conventional estimates. • Completed the first use of PARADIS dislocation dynamics simulations to calculate strengthening from precipitates in Mg (hcp) alloy (with LLNL). • Established methodology for modeling mechano-chemical driven phase transformations. • Used phase field crystal model to calculate grain boundary structures and energies in 2D and compared with molecular dynamics simulations. • Developed novel in-situ ultrasonic fatigue instrumentation to examine fatigue crack initiation and small crack growth in Mg alloys. • Demonstrated capability of digital image correlation for quantifying heterogeneous strain distributions within grains, at grain boundaries and adjacent to twins. • Demonstrated capability of crystal plasticity code to simulate tensile cracking at grain boundaries and fatigue crack propagation in polycrystals.

Structure/Property Relationships in Two-Phase f.c.c./B2 FeNiMnAl Alloys

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Funding: \$169,000 (2014)

PROGRAM SCOPE

The aim of this work is to develop an understanding of the microstructural stability and deformation mechanisms that control the strength of potentially-useful fcc/B2 FeNiMnAl alloys over a range of temperatures and strain rates. In addition, we are determining the origin of three particularly intriguing phenomena that we have found in FeNiMnAl alloys, i.e. 1. While $\text{Fe}_{25}\text{Ni}_{25}\text{Mn}_{30}\text{Al}_{20}$ shows no change in RT hardness upon annealing at 823 K for times up to 100 h, the related alloy $\text{Fe}_{30}\text{Ni}_{20}\text{Mn}_{30}\text{Al}_{20}$ shows a 45% increase in hardness when annealed over the same period with all of the increase occurring within the first 10 h. 2. $\text{Fe}_{28}\text{Ni}_{18}\text{Mn}_{33}\text{Al}_{21}$ fractures before yield under tension in the as-cast state, but exhibits increasing failure strains (up to 7%) as the microstructure coarsens (sic) and loses its blocky character upon annealing. 3. The elongation to fracture of the coarse, two-phase fcc/B2 alloy $\text{Fe}_{30}\text{Ni}_{20}\text{Mn}_{35}\text{Al}_{15}$ increases from 7% to 19% with increasing chromium additions (up to 6 at. %), with a concomitant decrease in the yield strength. The work involves: (1) Microstructural characterization of several two-phase fcc/B2 FeNiMnAl (with up to 6 at. % Cr) both after various heat treatments and after elevated temperature mechanical testing using a combination of state-of-the-art techniques and instruments. (2) Measuring the strength and ductility under tension as a function of temperature and strain rate after different heat treatments and for various Cr additions (up to ~6 at. %). (3) Determining the deformation mechanisms using a combination of post-mortem TEM dislocation analysis, post-mortem SEM fractography, TEM in-situ straining studies, and SEM in-situ straining studies. (4) Using the above results

to evaluate existing models of strength and ductility of similar microstructures and/or develop new models based on the experimentally-observed deformation mechanisms.

FY 2014 HIGHLIGHTS

The microstructure and mechanical properties of $\text{Fe}_{28}\text{Ni}_{18}\text{Mn}_{33}\text{Al}_{21}$, which consists of fine (50 nm phase width) B2 and fcc phases, have been studied in both the as-cast and annealed states. Upon annealing the fine aligned microstructure is replaced by a coarser microstructure, in which the phase size increased with increasing annealing time, up to ~2500 nm for a 250 h anneal. The as-cast alloy showed brittle fracture at room temperature, while the annealed materials all showed yielding before fracture, the elongation to failure increasing with increasing phase width. Tensile tests performed on $\text{Fe}_{30}\text{Ni}_{20}\text{Mn}_{35}\text{Al}_{15}$ with various Cr additions at a strain rate of $5 \times 10^{-6} \text{ s}^{-1}$ showed that even with a chromium additions as low as 0.5 at. %, the environmental embrittlement suffered by this alloy can be ameliorated: increasing Cr additions lead to a slow decline in room temperature yield strength but increasing elongation to values of 674 MPa and 18% elongation, respectively, at 6 at. % Cr. XPS showed that both Cr and Al form protective oxides at the surface and provide rapid passivation, thereby reducing hydrogen liberation rates on the surface and minimizing the environmental embrittlement. As-cast $\text{Fe}_{36}\text{Ni}_{18}\text{Mn}_{33}\text{Al}_{13}$ was cold-rolled to a thickness reduction of ~65% and then annealed at various temperatures from 1000-1273K for one hour. The hardness of the as-cast alloy is 193 HV, while that for the cold-rolled alloy followed by annealing at 1000K or 1273K was 412 HV and 250 HV, respectively. In room temperature tensile tests, the 1273K annealed material had an elongation of 21% (comparable to the as-cast material) but a 25% increase in yield stress to ~575 MPa. TEM examination shows this processing produced a fine-grained structure due to recrystallization. Oxidation tests performed on $\text{Fe}_{30}\text{Ni}_{20}\text{Mn}_{35}\text{Al}_{15}$ with and without 6 at. % Cr at 1073 K and 1273K showed that while all alloys showed excellent oxidation resistance, the Cr-modified alloy showed the better oxidation resistance.

Materials for Extreme Irradiation Environments

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

A common roadblock to the future-generation energy technologies proposed for high-efficiency energy production is the lack of materials that could function safely and economically in the envisioned harsh and aggressive in-service environments. This materials challenge is a daunting one, as required in-service conditions represent major departures from current systems, pushing materials into new domains, in particular, high levels of irradiation damage and high temperatures. In each of the DOE BES workshops on Basic Research Needs for Future Energy Technologies, it was recognized that current technologies could not be modified to provide the required order(s) of magnitude improvements in materials properties, and that a new paradigm was needed for designing, assessing and certifying new

materials. We proposed a new approach to design materials that are intrinsically resistant to irradiation and other extreme environments by utilizing nanostructuring and self-organization in these nonequilibrium systems. While we focus on nuclear applications, we expect that the scientific advancements achieved in this Cluster will have broad based significance for materials needs in a number of other advanced energy technologies. Our work will be directly related to the following two DOE-BESAC Grand Challenges: Characterizing and controlling matter away from equilibrium; Learning how remarkable properties emerge from complex correlations of atomic or electronic constituents and how we can control these properties. Our Cluster investigates the fundamental processes controlling the formation of novel, self-organized, nanostructured materials, their long-term structural and dimensional stability, and the relationships between the nanoscale features and the macroscopic properties. The research combines irradiation experiments, *in situ* and *ex situ* characterization of microstructure and properties, and atomistic simulations and continuum modeling.

FY 2014 HIGHLIGHTS

In FY 2014, we confirmed by atom probe tomography the stabilization by ion irradiation of compositional patterns and unique “cherry-pit” structures in the immiscible Cu-Fe and Cu-V alloys. We also demonstrated that irradiation-induced nanostructuring can take place in ternary alloy systems that form compounds, such as Cu-Si-Mo and Ni-W-C, thus greatly extending the range of alloy systems of interest. Interfaces play an essential role as point defect sinks for controlling the stability of these self-organized structures, but sink strengths are very rarely, and often only indirectly, measured. We overcame this issue by employing a novel marker broadening technique, which was applied to determine the sink strength of various Cu-X interfaces, X= Ni, V, Nb. We also investigated the mechanical properties of nanostructured alloys, using in-situ techniques. In particular we designed and validated a novel apparatus to measure the creep response of miniaturized metal pillars during high temperature irradiation. This apparatus made it possible to measure and compare the creep compliance of diverse materials, including CuTiAg metallic glass, Si, SiO₂, and Si₃N₄, and to isolate the contributions of electronic and nuclear excitations to irradiation creep. Furthermore, we used in-situ nanocompression tests in a transmission electron microscope to determine the strength of distinct Cu-Nb interfaces, revealing the contribution of interface crystallography and of irradiation-induced mixing on interface shear strength. On the modeling side, we investigated quantitatively the effect of lattice structure and strain fields on irradiation-induced segregation in alloys. These results were achieved by new and key extension to the so-called self-consistent mean-field model. This allowed us to couple first-principle calculations to phase field-type modeling of solute redistribution, for instance around dislocation cores, in specific alloy systems, including Ni-Si.

Characterization and Modeling of Deformation Induced Damage in Titanium Alloys

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Funding: \$195,000 (2014)

PROGRAM SCOPE

We are using a synergistic experimental and computational approach to identify and examine processes that cause damage nucleation at interfaces in two-phase $\alpha+\beta$ titanium (Ti) alloys. We have systematically studied two near α phase Ti alloys: $\text{Ti}_5\text{Al}_{2.5}\text{Sn}$ (wt.%), referred to as Ti525, and $\text{Ti}_8\text{Al}_1\text{Mo}_1\text{V}$ (wt%), referred to as Ti-811, and two two-phase $\alpha+\beta$ alloys: $\text{Ti}_3\text{Al}_{2.5}\text{V}$, referred to as Ti325, and $\text{Ti}_6\text{Al}_4\text{V}$ (wt.%), referred to as Ti-64, and compared the results with work on commercially pure (CP) Ti in order to determine how differences in composition and microstructure affect the processes that cause damage nucleation at interfaces at ambient and elevated temperature. We have characterized the deformation behavior and the preferential slip systems, as well as instances of slip transfer and grain boundary deformation behavior of this alloy, under a variety of loading rates and temperature and compared the results to single-phase α CP Ti. Using this knowledge to examine the deformation behavior in more complex and commercially important two-phase $\alpha+\beta$ Ti-alloy systems is the next objective. Future work will accomplish this objective using our unique combination of experimental techniques that allow the details of the deformation and fracture initiation mechanisms to be characterized in the context of the larger microstructure. Deformation in selected microstructure patches that are large enough to identify how neighboring grains influence stress shielding and strain incompatibilities will also be simulated using state-of-the-art polycrystalline plasticity-based finite element models. Successful completion of this research program will establish a paradigm by which the fundamental processes responsible for damage nucleation in polycrystals can be identified. The Ti alloys that will be examined are currently used in a wide range of aerospace structural applications, as well as within the energy generation, automotive, and biomedical industries.

FY 2014 HIGHLIGHTS

The momentum of this research program has continued in order to have sufficient data for statistical confidence in identification of deformation mechanism interactions with grain boundaries. The items listed below summarize important research accomplishments. (i.) Rules for slip transfer and damage nucleation across α/β boundaries have been investigated and a methodology for determining the CRSS ratios of different deformation modes has been developed based on in-situ observation of surface deformation traces made in a scanning electron microscope. (ii.) The relative activity of the different deformation systems changes as a function of alloying composition and deformation temperature was quantified. With increasing plastic deformation, the critical resolved shear stress (CRSS) variation at low and high strains has been observed, which may be the result of differently evolving hardening behavior in different slip systems, or other sources of uncertainty, which point toward valuable new areas for research related to statistical errors, rotations of grains during deformation, local stress state variation. (iii.) Effects of chemistry, temperature, and strain rate on slip heterogeneity have been identified (some quantitatively) from novel in-situ experimental methods. (iv.) Crystal Plasticity Finite Element Modeling (CPFEM) simulation show very good correlations with observed complex strain features in a real sample, making the local stress tensor, which is not experimentally measurable, available to evaluate local shear activity, which will lead to accelerated understanding of the driving forces for observed slip. (v.) The ability to image and characterize the dislocations at grain boundaries has been developed. The local dislocation density has been measured, which is related to the resistance of the grain boundary to strain transfer. (vi.) One PhD graduate student has finished his degree program. We have published two articles in peer reviewed journals and submitted two.

Granular Constraints and Size Effects in Polycrystalline Shape Memory Alloys

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

The primary objective is to study the granular and surface constraints on shape memory alloys in the transformation and elastic regimes. Experiments are carried out at the grain scale to see the effect of constraints imposed by neighboring grains on the grain of interest and how this affects the behavior of that grain under stress. Difference between bulk and surface constraints imposed by neighboring grains is also studied by using chemical etching to expose grains that were previously in the bulk to surface grains. The chief experimental technique for the same is High Energy X-Ray Diffraction Microscopy (HEDM). Separate surface studies are performed using Digital Image Correlation (DIC), which allows analyzing the surface of the material at a larger length scale. All samples analyzed have two holes drilled perpendicular to the axial loading direction of the sample, to model the “anti-micro pillar” experiments and also act as seed points for transformation of the material resulting from localized concentration of the stress field. These experimental results are then compared with Finite Element Analysis (FEA) to study the level at which continuum mechanics breaks down by confining different numbers of grains between the two micro holes. The sample is modeled using a continuum based polycrystalline constitutive model and the amount of deviation from experimental results shows where a micro-mechanical constitutive model is more relevant.

FY 2014 HIGHLIGHTS

Presented at SMST (Shape Memory and Superelastic Technology) Conference organized by ASM International in May 2014 at Pacific Grove, CA with a specific workshop on Shape Memory Alloy behavior. Conduction of experiments at Cornell High Energy Synchrotron Source, Cornell University and Argonne National Laboratory where monolithic (dogbone samples without machined microholes) as well as samples with two holes were analyzed using HEDM. This technique allows for 3D grain reconstruction to give individual spatial position and orientation of every grain, following which the effects of granular and surface constraints can be studied. Conduction of DIC experiments at Northwestern University and Colorado School of Mines for studying the transformation on the sample surface for three and two dimensional samples respectively. The two dimensional DIC is supported by Electron Back Scattering Detection (EBSD) results, which indexes individual grains with their orientation for planar surfaces. FEA analysis (both two and three dimensional) using the Stebner-Brinson continuum based model for comparison with experimental data to reach the breakdown of continuum assumptions, normalized to number of grains between constraining features (micro holes machined into the sample in this case).

Thermal Activation in Dislocation Dynamics of Face-Centered Cubic Metals

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Principal Investigator: Wei Cai

Sr. Investigator(s):

Students: 1 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)

Funding: \$228,500 (2014)

PROGRAM SCOPE

Dislocation dynamics controls plastic deformation, mechanical strength, and failure of crystalline materials. To date, thermally activated dislocation processes are still not well understood. The two most prominent thermally activated processes in pure Face-Centered Cubic (FCC) metals are: cross slip and forest cutting. Many fundamental questions regarding these two processes still remain open, and our proposed research seeks to provide answers. This project will use atomistic simulations with advanced sampling techniques, complemented by dislocation dynamics simulations, to determine the fundamental mechanisms of cross slip and forest cutting processes and their consequence on strain hardening. We will focus on the following four scientific questions. (1) How does the mechanism of homogeneous cross slip of an isolated screw dislocation depend on the various stress components? (2) What is the dominant mechanism of cross slip in a realistic dislocation microstructure? (3) What is the mechanism of forest cutting at finite temperature? (4) Is dynamic recovery controlled by cross slip or by thermally assisted removal of Lomer-Cottrell locks? The answers to these questions will represent a significant advance in our understanding of thermally activated dislocation processes fundamental to the deformation and microstructural evolution of metals, alloys and semiconductors. The knowledge gained in this research will be an essential component in the design and manufacturing of stronger, tougher and more damage-resistant materials for a wide range of future energy systems.

FY 2014 HIGHLIGHTS

(1) We successfully computed the energy barrier for cross slip of screw dislocations in FCC Ni as a function of three different stress components, using both the continuum line tension model and the discrete atomistic model. This is the first time the effect three relevant stress components on cross slip energy barrier are examined with atomistic detail. This work has been published in *JMPS* 62, 181, 2014. (2) We have developed more efficient time integrators for dislocation dynamics (DD) simulations, combining implicit integrators with subcycling algorithm. This leads to order-of-magnitude increase in the amount of strain that can be reached in DD simulations within a given computational time. This work has been published in *MSMSE* 24, 025003, 2014. (3) In an effort to understand the interaction between dislocations and solute atoms (a fundamental problem in controlling the strength of metals), we discovered a widespread error in the contemporary literature regarding the equilibrium concentration of point defects surrounding a dislocation (i.e. the Cottrell atmosphere). We show that the compressive self-stress inside existing inclusions must be excluded from the stress dependence of the equilibrium concentration of the point defects, because it does no work when a new inclusion is introduced. On the other hand, a tensile image stress field must be included to satisfy the boundary conditions in a finite solid. This work has been published in *JMPS* 66, 154, 2014. (4) PI Cai collaborated with colleagues in Universidad Campinus, Brazil, in the calculation of ideal shear strength (ISS) on the basal plane of HCP ^4He , a prototypical quantum solid, using path-integral Monte Carlo (PIMC) simulations. The failure mode upon reaching the ISS limit is characterized by the homogeneous nucleation of a stacking fault and it is found to be anisotropic, consistent with Schmid's law of resolved shear stress. This work has been published in *PRL* 122, 155303, 2014.

EARLY CAREER: Energetics of Radiation Tolerant Nanoceramics

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Funding: \$152,587 (2014)

PROGRAM SCOPE

Nanostructured materials are likely to play a large role in future nuclear reactors and radioactive waste storage due to their strength and potential resistance to structural damage from radiation. However, this potential is hindered by significant gaps in the understanding of interfaces' properties and their role in the overall performance of the nanocrystalline structures. The lack of reliable thermodynamical data of nanomaterials makes it extremely difficult to predict and fully exploit nanomaterials' properties in high-radiation environments, being one of the major reasons why the stability of the nanomaterials is still a big unresolved question. The goal of this project is to investigate nanomaterials with potential interest for nuclear components [the aluminate based spinels (MgAl_2O_4 , $M = \text{Mg, Ni, or Zn}$), and zirconia based materials (ZrO_2 doped with Y or Ca), and establish the link between composition, interface thermodynamics, and radiation resistance, aiming to enable a better understanding of the nature of enhanced performance in nanocrystalline ceramics. Nanoceramics (typically below ~ 100 nm) can show enhanced radiation resistance as compared to their bulk counterpart. This is hypothetically attributed to the increased interface areas in the form of grain boundaries that could act as effective sinks for radiation-induced defects, significantly hindering the accumulation of point defects. In this project, the mechanisms behind this phenomenon as well as its limitations considering the thermodynamics of nanomaterials are being unveiled by combining a series of sophisticated approaches, i.e.: (a) highly sensitive calorimetric techniques to provide a detailed thermodynamic description of the nanosystem; (b) advanced techniques for obtaining unprecedented nanocrystalline samples with grain sizes below 10 nm, (c) high energy ion irradiation studies, and (d) high resolution electron microscopy to study the defect profile.

FY 2014 HIGHLIGHTS

Development of novel synthetic processing and calorimetric techniques have been the initial outcomes of this project. This is because the project requires manufacturing of high quality nanocrystalline samples and techniques of high sensitivity to enable a comprehensive description of the system (that allows more reliable data analysis). Because those techniques were not available in the literature, the developments from this grant resulted in a large number of high-impact publications. The methods have consequences in diverse fields other than radiation tolerance, as they enable controlled fabrication and thermodynamic analysis of nanoceramics. The novel techniques culminated in a very important paper recently published in Scientific Reports (Nature Publishing Group). In that, the high-quality sample enabled an unprecedented solid description of radiation effect in nanocrystalline zirconia, with detailed correlation between kinetics and thermodynamics of radiation-induced defects. The paper is a landmark in the field that will set the stage for better understanding of radiation on nanomaterials.

EARLY CAREER: Deformation and Failure Mechanisms of Shape Memory Alloys

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Funding: \$150,000 (2014)

PROGRAM SCOPE

The goal of this research is to understand the fundamental mechanics driving the deformation and failure of shape memory alloys (SMAs). SMAs are difficult materials to characterize because of the complex solid-to-solid phase transformations that give rise to their unique properties. These phase transformations occur across multiple length scales and result in a large hysteresis loop, which allows these materials to store or dissipate substantial amounts of energy. In order to optimize the use of this hysteretic behavior in energy storage and damping applications, we must first have a quantitative understanding of the transformation behavior. New methodologies have been used to provide the first quantitative, full-field characterization of phase transformation across multiple length scales, with a focus on the relationship between microstructure and transformation. The proposed research is important from both a fundamental and a practical standpoint. SMAs are an excellent example of the fact that nearly all materials are dependent on multi-scale interactions, and the lessons to be learned from these experiments are representative of a wide class of materials. Here, atomic interactions, sub-granular transformation, intra-granular interactions, localized strain banding, and macroscopic behavior are all closely linked. The quantitative, spatially resolved information resulting from this research is especially useful to the numerous theoretical and computational studies of SMAs that are currently underway. In addition, the new experimental methodologies that have been developed as part of this research are applicable to a wide range of future investigations into the mechanics of strain localization. Finally, these experiments have produced results that significantly elucidate the change in the underlying mechanisms of phase transformation at small length scales.

FY 2014 HIGHLIGHTS

In the past year, work has focused on the statistical analysis of small-scale experimental results. This analysis has produced new findings that are directly applicable towards the modeling and prediction of shape memory alloy behavior. We have determined that contrary to a common assumption in mean-field theories, grains of similar orientation (a) do not necessarily transform similarly; and (b) that a single preferred variant does not nucleate and subsume entire grains. Rather, we quantified large degrees of transformation heterogeneity and extent in similarly oriented grains, including the identification of specific and distinct martensite laths. These findings have recently been submitted for journal publication. Another journal publication in progress details the quantitative interactions between plasticity and transformation on a grain-by-grain basis, and their dependence on cycling and microstructural neighborhood. Interestingly, a certain degree of residual strain (locked in martensite and plasticity) can in fact assist subsequent phase transformation, likely through the action of dislocation networks. At larger length scales, macroscopic fracture studies have been performed to examine the dependence of crack tip shielding (by phase transformation) on strain rate and crystallographic texture, aiming to address a lack in both dynamic and local data on superelastic shape memory alloys. A custom J-integral code that utilizes both line integral and area integral calculations of digital image correlation

data was successfully used to examine dependence on strain rate. These studies are currently being extended to a wider range of strain rates and to include microstructural factors.

Mechanical and Fracture Behavior of Molecular-Reinforced and Hybrid Glasses

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Funding: \$220,000 (2014)

PROGRAM SCOPE

Our research is focused on fundamental studies related to the molecular design, synthesis, characterization and modeling of molecular-reinforced hybrid glass films for superior mechanical and fracture properties in hostile chemical and UV radiation environments. Molecular-reinforced hybrid glass films exhibit unique electro-optical properties while maintaining excellent thermal stability. They have important technological application for emerging nanoscience and energy technologies including anti-reflective and ultra-barrier layers in photovoltaics and display technologies, microelectronic interlayer dielectrics, optical waveguides, and high-performance coupling layers in structural laminates. However, they are often inherently brittle in nature, do not adhere well to adjacent substrates, and exhibit poor mechanical properties. Our research brings together a unique combination of internationally recognized thin-film processing and mechanical characterization capabilities coupled with computational modeling that we have pioneered to study hybrid films. We have developed high-productivity capabilities for sol-gel fabrication together with newly developed atmospheric plasma deposition to inexpensively synthesize hybrid films. Composition and molecular structure is characterized using high resolution X-ray, electron, optical and nuclear spectroscopies. Mechanical properties are studied using acoustic, nanoindentation, force modulated AFM, and thin-film adhesion and cohesion techniques we have pioneered for thin-film structures. Furthermore, we leveraged computational modeling capabilities that have allowed us to understand the complex elastic properties of hybrid molecular materials. This has enabled the molecular design, synthesis, characterization and modeling of hybrid films for superior mechanical and fracture properties in hostile chemical and UV radiation environments.

FY 2014 HIGHLIGHTS

Highlights of our research include developing an atmospheric plasma technique to deposit hard, adhesive, and highly transparent dense hybrid bilayer coatings on plastic substrates in ambient air, at room temperature, in a one-step process, using a single precursor. The adhesion of the hybrid films to the polymer substrates was significantly improved by forming a hybrid glass film with carbon-bridges that provide a molecular reinforcement of the film, and strong bonding to the underlying polymer. A hard dense hybrid layer was subsequently deposited on top of the underlying film. The bilayer structure exhibited ~100% visible transmittance, twice the adhesion energy and three times the Young's modulus of commercial polysiloxane sol-gel coatings. Hybrid molecular materials containing both organic and inorganic components and synthesized via sol-gel chemistry exhibit unique and superior mechanical properties. In our research we recently unraveled the underlying hydrolysis and condensation reactions of an epoxy-silane and metal alkoxide precursor to deposit moisture-insensitive hybrid organic/inorganic

films via dip coating. We have now also demonstrated a new spray sol-gel processing technique to deposit hybrid organic/inorganic films with a compositionally-graded structure with excellent adhesive properties. Finally, we leverage computational models to demonstrate the existence of asymmetrical elastic behavior of hybrid organic-inorganic glasses. The existence of asymmetrical elastic behavior has significant effects on thermomechanical stresses and reliability but has never been demonstrated. We have developed computational tools to generate a highly accurate molecular model of an organosilicate glass and report the first indication that they display asymmetric elastic behavior, a rare property for any material. Initial results indicate that a difference in free volume under compressive and tensile states underlies the asymmetry for the partially connected networks.

Inferring Grain Boundary Properties from Measurements on Grain Boundary Networks

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Funding: \$300,000 (2014)

PROGRAM SCOPE

The goal of this project is to build analysis tools that infer accurate and general grain boundary (GB) crystallography-property relations with quantified uncertainty by assembling partial but complementary data readily obtainable with existing experimental and modeling methods. These tools will markedly enhance our ability to predict and control—through computational design—materials properties governed by GB networks, such as intergranular fracture, diffusion, and embrittlement. We have adopted gallium permeation through GB networks in Al as a model problem on which to develop and validate these tools. The crux of this project is integration of information obtainable from easy-to-perform experiments and simulations. GB properties depend, at minimum, on five crystallographic variables. Conventional approaches, such as investigation of individual GBs using electron microscopy or atomistic modeling, provide incomplete information concerning GB crystallography-property relations. However, the information provided by many of these techniques is complementary. This project integrates information available from multiple sources using analytical techniques such as Bayesian inference and GB network analysis to obtain a more complete understanding of GB crystallography-property relations in a resource-efficient way.

FY 2014 HIGHLIGHTS

We developed methods to track Ga permeation *in situ* in a scanning electron microscope and to relate it to the full five-parameter GB character, obtained through two correlated electron backscatter diffraction measurements. Within a single permeation experiment, we can distinguish between high diffusivity paths as well as clusters of GBs that are either not permeated at all or at a much slower rate. These experiments give qualitative insights into GB crystallography-property relations for Ga permeation into Al, e.g. that Ga permeation velocity does not scale with GB misorientation angle for high angle, general GBs. To infer quantitative GB crystallography-property relations, we have made theoretical advances in the complementary tasks of homogenization (calculating aggregate properties from GB behavior) and localization (calculating GB properties from aggregate behavior). We demonstrated that

the Generalized Effective Medium homogenization scheme provides quantitatively accurate predictions of aggregate diffusivity, D_{eff} , in GB networks with diffusivity contrast ratios from 10 to 10^8 . We then solved the inverse problem of localization by deducing the local diffusivity of each boundary with given microstructure data and measurements of D_{eff} from simulations. Finally, we are using Bayesian inference to integrate macro-scale measurements on GB networks with atomistic and mesoscale simulations as well as data available in the literature. This approach requires a “likelihood model” that predicts the probability of observing a specific Ga permeation rate given a specific permeation mechanism. We formulate this likelihood model using the phase field method. GBs are modeled as surfaces with non-uniform energy and Ga concentration in a GB is described using an order parameter that obeys the Cahn-Hilliard equation. By modifying the gradient energy penalty parameter in this equation, we describe permeation mechanism ranging from Fickian diffusion to front propagation.

Designing Nanoscale Precipitates in Novel Cobalt-based Superalloys to Improve Creep Resistance and Operating Temperature

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Funding: \$50,000 (2014)

PROGRAM SCOPE

This ongoing research program focuses on the investigation of a novel family of Co-Al-W-base alloys for use in high-temperature structural applications. These alloys contain a high volume fraction of coherent $\gamma'(L1_2)$ -precipitates with the composition $Co_3(Al,W)$ that obstruct the motion of dislocations, providing high strength at both ambient and elevated temperatures. This is analogous to the Al-Sc-X system (with strength provided by α' - $Al_3(Sc,X)$ precipitates) and the Ni-Al-Cr-based systems (with γ' - $Ni_3(Al,Cr)$ precipitates). We will expand upon our fundamental studies of several representative Co-based superalloys (ternary Co-Al-W, quaternary Co-Al-W-Ni, and higher alloyed specimens containing Ti, B, and/or Zr to enhance the γ' -solvus temperature and grain-boundary strength), focusing on the stability of the strengthening γ' -precipitates and their contribution to strength at ambient and elevated temperatures. The improved creep- and coarsening-resistance of the Co-Al-W system is anticipated to enhance the operating temperature of land-based turbines and jet engine components by 100-150 K compared to those of contemporary Ni-based superalloys, resulting in improvements in engine efficiency and a reduction in fuel consumption, operating costs, and emissions. Our overarching goal is to achieve, on a fundamental level, an understanding of and predictive capability for the $\gamma'(L1_2)$ - $Co_3(Al, W)$ phase stability, morphology, and how these and other factors contribute to mechanical strength of the alloy. We will investigate the stability and microstructural evolution of the γ' -phase during nucleation, growth, and coarsening of precipitates, and their effect on strength at both ambient and elevated temperatures.

FY 2014 HIGHLIGHTS

During this fiscal year, our efforts have been focused on expanding upon our initial work regarding alloying effects on the microstructure and mechanical behavior of these alloys. Specifically, the addition

of sufficient quantities of boron to the ternary alloy leads to the formation of large W-rich borides, whose composition has been measured via atom probe tomography (APT). The presence of these borides has a strong effect on the creep strength of the alloy, decreasing the minimum steady-state strain rate by two orders of magnitude compared to the boron-free alloy, but results in a precipitate denuded zone along the grain boundary that decreases the yield stress at room temperature. We have also built upon our current understanding of quaternary alloying effects, investigating the impact of Ru and Ti additions on the morphological and compositional evolution of the $\gamma + \gamma'$ microstructure during isothermal aging. Ru, an important alloying element for recent-generation Ni-base superalloys, destabilizes the $\gamma + \gamma'$ microstructure during extended isothermal aging due to the onset of discontinuous transformation initiated at the grain boundaries. Alloys containing both Ti and B exhibit improved creep properties compared to ternary Co-Al-W, but the improvement is limited by the dearth of strengthening borides observed during our concurrent investigation of the Co-Al-W-B and Co-Al-W-B-Zr systems; investigation via APT has revealed that in the case of the Ti and B containing alloy, boron partitions to the γ' phase limiting segregation to the grain boundaries. DFT calculations on a ternary Co-Al-W system predicted that the anti-phase boundary (APB) energetics for g' (100, 111, and 111/100 anisotropy) are comparable to that of Ni_3Al . In addition, it was found that $\text{Co}_3\text{Al}_{0.5}\text{W}_{0.5}$ solid solution APB energies are not merely an average of the Co_3Al and Co_3W energies, and negative APB energies calculated for Co_3Al reflect thermodynamic metastability of the Co_3Al $L1_2$ structure.

Response of Simple, Model Systems to Extreme Conditions

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

The emphasis of the proposed research is on the application of high-pressure/high-temperature techniques, together with intense energetic ion beams, to the study of the behavior of simple oxide systems (e.g., SiO_2 , GeO_2 , and Ln_2O_3) under extreme conditions. These simple stoichiometries provide unique model systems for the analysis of structural responses to pressure up to and above 1 Mbar, temperatures of up to several thousand Kelvin, and the extreme energy density generated by energetic heavy ions (tens of keV/atom). The investigations will include systematic studies of radiation- and pressure-induced amorphization of high P-T polymorphs. We will apply state-of-the-art *in situ* synchrotron diffraction techniques together with advanced transmission electron microscopy to characterize the different structural modification, which includes crystal-amorphous and crystal-crystal phase transformations. Through an extensive network of collaborations, we have access to a wide variety of experimental facilities including large ion accelerators and synchrotron beamlines. By studying the response of simple stoichiometries that have multiple structural “outcomes”, we will establish the basic knowledge required for the prediction of the response of more complex structures to extreme conditions.

FY 2014 HIGHLIGHTS

The temperature dependence of track formation was studied in natural SiO₂ samples up to 913 K. SAXS revealed an increase in the ion track radius of approximately 0.1 nm per 100 K increase in irradiation temperature. MD simulations and thermal spike calculations are in good agreement with these values and indicate that the increase in track radii at elevated temperatures is due to a lower energy required to reach melting of the material. The shape of single ion tracks was estimated by a combination of SAXS measurements on track radii in apatite and SRIM calculations of the dE/dx. The apparent cigar-like shape with the cross-section reaching its maximum at the last quarter and decreasing rapidly towards the end of the track results from a combination of the varying dE/dx as well as energy density (velocity effect) when the ion penetrates the material. Irradiation-induced modifications were systematically investigated for Ln₂O₃ materials in the cubic bixbyite phase as a function of ion fluence using synchrotron x-ray micro-diffraction. In response to irradiation with 185 MeV Xe ions, the light lanthanide sesquioxides (Sm₂O₃, Gd₂O₃, and Ho₂O₃) were amorphized, while irradiation with 2.2 GeV Au ions induced a transformation to the monoclinic high temperature polymorph. In contrast, the heavy compounds (Tm₂O₃, and Lu₂O₃) underwent a transformation to a nonequilibrium cubic phase under both irradiation conditions. This phase was found to be isostructural with the high temperature cubic polymorph of La₂O₃, which is known to be a fast ion conductor and has not previously been observed for these compounds. The response of coupled extreme conditions was studied by irradiating dense 6-fold coordinated GeO₂ glass *in situ*, i.e., at a pressure of 45 GPa, with swift heavy ions that were injected into a diamond-anvil cell. The application of pressure and high-energy deposition from ions in tandem induced an amorphous-to-crystalline phase transition.

Grain Boundary - Dislocation Interactions in Polycrystals: Characterization and Simulation for the Effective Design of High-Strength, High-Ductility Structural Alloys

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Funding: \$616,999 (2014-2016)

PROGRAM SCOPE

A breakthrough capability to mathematically treat trillions of line defects in crystals, called dislocations, will be developed and verified. Novel experiments, analysis, and simulation of dislocations interacting with crystal plane defects, called grain boundaries, in copper and tantalum will be carried out. The results will be incorporated in a super-dislocation (SD) model, thus introducing a dimension of materials design heretofore unavailable. Success will allow development of new polycrystalline alloys with improved strength and ductility. More broadly, the techniques established will be suitable for treating many types of dislocation interactions in a wide variety of metallic materials. Three enabling technologies will be created and used to accomplish the objectives: 1. At the meso, or middle, scale, new “meso-dislocation microscopy” will measure critical meso-scale quantities. 2. At the atomic scale, “high-throughput molecular dynamics” will be constructed to simulate large numbers of defect interactions. 3. At the macro scale, a “super-dislocation model” will analyze evolving populations of

dislocations. Careful comparative analysis of the three sets of results will reveal the fundamental mechanisms and linkages among the scales that control the properties of polycrystalline alloys.

FY 2014 HIGHLIGHTS

This financial year covers a single month of the new project. However, some progress has been achieved in all three enabling technologies: 1. Dislocation microscopy has been performed on a large-grained aluminum alloy as a proof of concept for the planned experimental work. The expected build-up of dislocation density at grain boundaries was observed. 2. Initial atomistic simulations have been undertaken to demonstrate the capability of simulating the nucleation of dislocations close to grain boundaries. This capacity will be fundamental to all future atomistic modeling tasks. The majority of effort has been spent on determining the ideal methods by which to measure the critical metrics that accurately describe dislocation-defect interactions. 3. Collaboration has begun with Sandia National Laboratory to co-develop the super-dislocation model. Furthermore, an ideal candidate for the post-doctoral position at Ohio State University has been identified; he will begin work on the model in 2015. A project meeting with collaborators at Sandia National Laboratory was scheduled, and occurred after the end of the fiscal year.

Atomic Scale Computational and Experimental Investigation of Twinning Mechanisms in HCP Systems

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Funding: \$434,980 (2014-2016)

PROGRAM SCOPE

Increasing both strength and ductility is the ultimate achievement for most structural materials. Traditional methods for strengthening rely on controlled generation of internal defects, and thereby increase strength at the cost of reducing ductility and toughness. Various levels of ductility are observed in hcp metals and their alloys: from extensive ductility in Ti and Zr to poor ductility in Mg, Zn and Be. Understanding the mechanisms behind this divergent behavior is important from both theoretical and industrial application points of view. Low temperature ductility of hcp metals is linked to twinning – an important deformation mode where the number of active slip systems is limited. In extensively ductile Ti and Zr, more than one twin system is operative in both tension and compression while less ductile metals, such as Mg, twin mainly in one mode (the most common being the (10-12) system). Our goal is to understand the fundamental reasons underlying the different twinning behavior of various hcp metals by comparing twin nucleation and growth mechanisms in Ti and Mg and their alloys. Of particular interest is the effect of alloying on twin nucleation and growth which, until now, has not been rigorously quantified. To achieve this goal, we will use a combined computational and experimental approach; deformation mechanisms at individual-defect-scale are best captured through computational methods. Experimental studies have been able to determine characteristic features of twins such as their crystallography, twin shear as well as the strain rate, stress or temperature under which twins form. However, observed twins are usually several nanometers to micrometers thick based on optical or SEM-level analysis, making it impossible to capture atomic scale processes responsible for their nucleation.

FY 2014 HIGHLIGHTS

The project start date is August 2014. The graduate student sponsored by this project has joined OSU and started to work on this project in September 2014.

EARLY CAREER: Modulating Thermal Transport Phenomena in Nanostructure via Elastic Strain at Extreme Limits of Strength

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Funding: \$155,000 (2014)

PROGRAM SCOPE

Nanoscale materials fabricated with nearly pristine crystal structure are often endowed with ultra-strength behavior, where material failure occurs at a significant fraction of its ideal limit. The thermal conductivity exhibited by such materials is also uniquely affected by the high surface-to-volume ratio at the nanoscale. The juxtaposition of the vastly increased dynamic range of elastic strain available in ultra-strength nanomaterials and altered thermal transport shows promise for tunable thermal properties. This project aims to exploit these properties of high-strength nanostructures to elucidate the coupling between large mechanical strains and thermal conductivity (both electron and phonon) leading to better understanding and control of the thermal performance in these materials. Unique fabrication methods to produce nanosized quasi-defect free single crystals and modern nanomechanical testing will be used to identify the size-dependent dynamic range of elastic strain and understand deformation mechanisms near the ideal limit. Identifying and quantifying thermal transport phenomena as a function of mechanical strain in these nanostructures will open the door to using elastic strain engineering in high-strength nanomaterials to tune thermal transport. The results of these investigations will be used to improve the performance, efficiency, and versatility of advanced thermal management and energy conversion devices with tunable response.

FY 2014 HIGHLIGHTS

Supported by this DOE program, we recently developed a novel *in situ* approach and reported on the first experimental measurements demonstrating the effect of both spatially uniform strain and nonuniform strain resulting from defects on thermal conductivity of an individual Si nanowire using a method that we term *in situ* Raman piezothermography. Our results show that, whereas phononic transport in undoped Si nanowires is largely unaffected by uniform elastic tensile strain, a nonuniform strain field introduced via ion bombardment reduces the thermal conductivity by over 70%. In addition to discerning surface- and core-governed pathways for controlling thermal transport in phonon-dominated insulators and semiconductors, we expect our novel approach to have broad applicability to a wide class of functional 1D and 2D nanomaterials. Motivated by our results on Si nanowires and the strong observed role of strain heterogeneity, we have also developed a novel and generic strategy for tunable thermal and electronic transport in Si nanomeshes (thin films with patterned pore arrays). We exploit nanoscale patterning of a periodic mesh structure and spatially varying elastic strain gradients to locally modify electronic band structure and phononic behavior in a manner beneficial to electron and

thermal transport. In analogy to periodic artificial structures and atomic-level defects that introduce elastic strain gradients owing to perturbations of the otherwise perfect crystalline lattice, we term these structures metadefects. Experimental realization of these effects has also been pursued, with guidance and optimization from full-field modeling. We have developed and implemented a micro- and nanofabrication process flow to prototype Si nanomeshes based on silicon on insulator wafers. Mechanical, electronic, and thermal characterization of these samples is currently underway.

EARLY CAREER: Investigation of Radiation Damage Tolerance in Interface-Containing Metallic Nano Structures

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Funding: \$150,000 (2014)

PROGRAM SCOPE

The project seeks to conduct a basic study by applying experimental and computational methods to obtain quantitative influence of helium sink strength and proximity on He bubble nucleation and growth in He-irradiated nano-scale metallic structures, and the ensuing deformation mechanisms and mechanical properties. The proposed work utilizes a combination of nano-scale in-situ tension and compression experiments on low-energy He-irradiated samples combined with site-specific microstructural characterization and modeling efforts. This systematic approach will provide us with critical information for identifying key factors that govern He bubble nucleation and growth upon irradiation as a function of both sink strength and sink proximity through an experimentally-confirmed physical understanding. So far, the attention has been focused on studying individual bcc/fcc interfaces within a single nano structure: a single Fe (bcc)-Cu (fcc) boundary per pillar oriented perpendicular to the pillar axes, as well as pure bcc and fcc nano structures. Additional interfaces of interest include bcc/bcc and metal/metallic glass all within a single nano-structure volume. The model material systems are: (1) pure single crystalline Fe and Cu, (2) a single Fe (bcc)-Cu (fcc) boundary per nano structure (3) a single metal-metallic glass, all oriented non-parallel to the loading direction so that their fracture strength can be tested. A nano-fabrication approach, which involves e-beam lithography and templated electroplating, is utilized, which enables precise control of the initial microstructure control. Experimentally determined stress-strain relationships are enhanced by in-situ SEM observations coupled with TEM microstructural characterization of the same samples before and after deformation (irradiated and as-fabricated) and atomistic (MD) modeling.

FY 2014 HIGHLIGHTS

Tensile specimens shaped as cylinders with "hats" for gripping have been fabricated from the following material systems: (1) Amorphous Ni-P metallic glass, (2) Amorphous Fe-W metallic glass, and (3) Single crystalline Fe. The diameters of these specimens are between 50nm and 100nm have been fabricated, irradiated, and mechanically tested. In addition multiple free-standing "nano-walls" were produced to extend the perimeter and area between the two adjoining material and to help understand the interfacial topology and its effect on radiation damage. Monolithic Ni-P Fe (irradiated and as-fabricated) nano structures with diameters of ~75-100nm were tested in uniaxial tension (in-situ). This diameter

was chosen intentionally to achieve electron transparency during TEM analysis so that He bubbles could be readily observed.

Nanoscale Characterization of Intragranular and Intergranular Deformation Mechanisms

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Funding: \$500,000 (2014-2016)

PROGRAM SCOPE

Having developed the tools necessary to characterize stress-assisted room temperature grain growth in nanocrystalline metals, we are now expanding our study to quantify, locally and at the nanoscale, the influence that stress concentrations and microstructural details have on the deformation behavior of microcrystalline metals and alloys. To be truly predictive, multi-scale models and descriptions of deformation processes must be based on experimentally identified physical mechanisms and benchmarked at salient length scales. Our work offers unique opportunities to advance both nanoscale characterization and benchmarking. Two new experimental techniques, TEM-based precession-assisted crystal orientation mapping (PACOM) with Topspin AutoSTRAIN acquisition & analysis and SEM-based transmission Kikuchi diffraction (TKD), offer unprecedented spatial resolution and the opportunity to map, with 2-3nm step sizes, lattice distortions, stress concentrations, and dislocation populations. These techniques are being employed to identify active deformation mechanisms and collect local measures of structure, orientation, and stress that can be used to elucidate nanoscale details such as: the role of local stress concentrations in nascent twin formation in polycrystalline Mg and Zr; the redistribution of local stress during grain boundary migration, twinning, and dislocation pileups; and the storage of geometrically necessary dislocations during plasticity.

FY 2014 HIGHLIGHTS

In 2014 our research focused on *in situ* experiments conducted on nanocrystalline copper. Freestanding films were deposited and annealed at 400°C to produce an equiaxed microstructure (average grain size ~70nm) with extensive growth twins; these films were strained and characterized using precession-assisted crystal orientation mapping (PACOM). The goal of these tests was to observe stress-assisted grain boundary migration (GBM). Indeed, GBM was observed in these films, but it was not the dominant deformation mechanism as has been observed in other materials. We found that GBM and corresponding grain growth occurs by the movement of random boundaries by small amounts, which results in the growth of some grains and the annihilation of others. The mechanism does not rely on a subset of boundaries with a specific character that allows them to have high mobility. There is also no correlation between the out-of-plane texture of the grains and their propensity to grow at the expense of their neighbors. In addition to GBM we were also able to observe extensive deformation twinning and dislocation activity. Among grains near the crack tip where stresses are high there are many instances of coherent $\Sigma 3$ twin boundaries nucleating at a grain boundary, propagating across a grain, and then increasing in width. Both bright-field TEM imaging and intragranular misorientations determined with PACOM suggest that dislocations are active in larger grains and are responsible for plastic deformation. While the angular resolution for the PACOM setup used in the last round of experiments was not

sufficient to measure local variations in strain (and, as a result, dislocation density) within grains, we now have installed software that will allow us to do so. This will enable us to observe how dislocation populations can enable or inhibit other mechanisms such as twinning as well as measuring how dislocation structures evolve throughout deformation.

Stability of High-Strength Nanocrystalline Structures

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Funding: \$17,017 (2014)

PROGRAM SCOPE

Numerical simulations at nanometer scale have advanced the understanding of plastic deformation. Unfortunately, simulations that resolve these length scales constrain the deformation regime to high strain rates. Extrapolating numerical predictions to experimental conditions remains an unresolved challenge. The goal of this program is to study deformation mechanisms in nanocrystalline and ultrafine crystalline materials over a wide range of strain rates. In particular, we study plastic strain recovery upon unloading, reverse plastic strain during cyclic loading and the strain rate sensitivity of the collective behavior of partial and extended full dislocations.

FY 2014 HIGHLIGHTS

We find that the strain rate has a significant impact on the nucleation of leading and trailing partial dislocations. At high strain rates the density of leading partials and consequently, the density of stacking faults, grows initially and later decreases as the deformation proceeds. At the same time the density of extended full dislocations shows a monotonic increase with the applied strain. Finally, the density of extended full dislocations grows beyond the density of partial dislocations as the deformation accumulates. We have studied reverse plastic strain during cyclic loading and plastic strain recovery upon unloading with dislocation dynamics simulations. We vary the average grain size, the grain size distribution and the loading conditions to understand the effect of the microstructure and the loading history. To simulate thermally activated plastic strain recovery upon unloading we coupled dislocation dynamics simulations to a kinetic Monte Carlo algorithm. Our simulations give further evidence that reverse plastic strain during cyclic loading occurs as a consequence of the formation of dislocation structures due to the interaction of dislocation with grain boundaries in agreement with experiments. During re-loading a reverse motion of dislocations is observed in the simulations. Dislocations are annihilated during reverse motion reducing the dislocation density and the plastic strain. Increasing the heterogeneity of the microstructure increases the amount of reverse plastic strain until it reaches a plateau. This shows that reverse plastic strain is driven by stress inhomogeneity due to distributions of grain sizes but also by stresses due to the formation of dislocation structures in larger grains that are able to store dislocations that are annihilated during unloading.

Understanding Microplasticity Processes Related to Fatigue Damage Using High Energy X-Rays and a Crystal-Based Modeling Formulation

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Funding: \$750,000 (2014-2016)

PROGRAM SCOPE

Predicting fatigue crack initiation in ductile polycrystalline materials remains one of the materials science's most important unsolved problems. Generations of researchers have agreed that during low cycle fatigue conditions, spatially heterogeneous cyclic plasticity lies at the core of microcrack initiation. Understanding the conditions that cause plastic deformation to transform to microcracks in a polycrystal remains elusive. During the first three years of this grant, our team has built a hybrid experimental / computational capability to “watch” cyclic plasticity at the scale of each individual grain within a deforming polycrystal. Diffraction patterns from crystals within a deforming polycrystal are used to inform micromechanics-based finite element simulations. X-rays are projected through the model and its performance is examined by comparing the diffracted intensities measured on the virtual and real detectors. During the current project, we are implementing the new methodology to examine the formation of persistent slip networks (PSNs) – polycrystalline analogs to persistent slip bands formed in single crystals. We believe that PSN becomes configured to fully accommodate the macroscopic plastic strain amplitude applied to a specimen or engineering component. The formation of the PSN occurs over many cycles, but eventually this highly localized region is transmitting such an enormous flux of reversed plasticity, that fissures and voids eventually form and microcracks initiate. The objectives of this project are to explore the hypothesis that PSNs exist within polycrystals subjected to low cycle fatigue conditions and that there exists a threshold plastic strain amplitude beyond which PSN formation and eventual microcrack initiation is inevitable.

FY 2014 HIGHLIGHTS

Our new project began in February, 2014. During these first several months we examined the structure of the polycrystal model relative to the cyclic response observed in the diffraction data from. In particular, a latent hardening constitutive model was implemented to capture the tension-compression asymmetry observed in the full width at half maximum (FWHM) diffraction data. We also investigated the effect of crystallographic neighborhood on the diffraction results. In order to be consistent with legacy fatigue data, we also transitioned from a copper alloy (OMC copper) to “pure” OFHC copper. Preliminary experiments were conducted on the OFHC material. Finally, we constructed a more sophisticated mosaic diffraction model to better understand the relationship between heterogeneous slip and FWHM.

Transformation and Deformation Mechanisms in High Temperature Shape Memory Alloys with Nanoprecipitates

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Funding: \$203,994 (2014)

PROGRAM SCOPE

The focus of this program is on an emerging class of high temperature shape memory alloys (HTSMAs) that are exciting candidates for actuators and adaptive components in a wide range of energy and transportation applications. These HTSMAs offer the possibility of high reliability, lighter weight and increased capability while lowering space and power consumption. However, at present there is only elementary understanding of the important microstructure-property relationships. The goals of this effort therefore are to (1) develop a fundamental understanding of the inherent microstructure-property behavior of high temperature shape memory alloys and (2) develop computational models that capture these structure-property relationships and provide novel insights into the important transformation and plasticity mechanisms that govern their behavior. Two “Ni-rich” HTSMA alloy systems are at the core of the effort: Ni(Ti,Hf) and (Ni,Au)Ti alloys can exhibit high transformation temperatures, large transformation strain and small permanent strain. These beneficial properties can be strongly influenced by the formation of nanoscale precipitates. Spearheaded by advanced characterization techniques, and aided by insights from first principles modeling, the unusual and novel atomic structure and composition of these precipitates is being determined, along with their coherency with the matrix. Interaction of precipitates with martensite at lower temperature and dislocation activity at higher temperature are key mechanistic insights being sought through *in situ* electron microscopy studies, and being understood through new phase field modeling approaches to particle/defect interactions. These insights are being incorporated into a microstructural finite element framework in order to capture how phase transformations, crystal plasticity, and time-dependent creep interact to determine the response of single crystal micropillar experiments.

FY 2014 HIGHLIGHTS

Research in the past year has focused on understanding and modeling the effect of aging and formation of H-phase precipitates on the martensite transformation and plasticity in the Ni-Ti-Hf system. Mechanical testing has revealed the dramatic effect of aging on the critical stress for transformation/plastic flow as a function of deformation temperature in several near-stoichiometric compositions. At short aging times, a distinct precursor to the H-phase (H') has been determined. The nature of H' and H-phase precipitates, as well as the interface between and the high temperature austenite and lower temperature martensite matrix has been further studied using HAADF imaging. The effects of H-phase precipitation on martensitic transformation and shape memory properties has been modeled through a new, coupled phase field/finite element method (FEM) model that is capable of simulating transformation and plasticity as a function of precipitate structure. The results of the modeling are helping to rationalize the complex effects of aging on transformation and mechanical behavior. A new thrust on the Ni-Ti-Au system has also begun and preliminary microstructure analysis

has been completed. This system is remarkable since it has the highest transformation temperature while providing attractive actuation work output under load-bias, thermal cycling conditions. However, it is also very unusual since its mechanical behavior is only modestly affected by deviation from stoichiometry or aging condition. The microstructure origins for this behavior, which is in such sharp contrast to that seen in Ni-Ti-Hf, are presently under investigation. A final thrust has involved initial study of an extraordinary grain refinement that occurs under load-bias thermal cycling conditions in binary NiTi. The grain refinement has been identified for the first time through a combination of *in situ* TEM heating experiments and ASTAR grain mapping measurements.

Fracture Mechanisms and Fatigue of Magnetic Shape-Memory Alloys

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Funding: \$30,000 (2014)

PROGRAM SCOPE

Fracture resistance and long fatigue life are required to commercialize Ni-Mn-Ga ferromagnetic shape memory alloys. While Ni-Mn-Ga achieves high fatigue life at low strains, there is little data on the fatigue life of samples that are actuated near the theoretical strain limit. Furthermore, constraints imposed by clamping samples impact their magneto-mechanical and fatigue properties. Here, 10M Ni-Mn-Ga single crystals were exposed to a rotating magnetic field while holding them with rubber O-rings so they were not constrained. Prior to testing, sample surfaces were prepared to various levels of surface roughness. Fatigue life varied with some samples reaching more than 800,000 cyclic loads before fracturing and some samples failing after only 4,000 cyclic loads. Long fatigue life and fracture resistance are achieved when avoiding crystal defects and surface imperfections. Short fatigue life was caused by high surface roughness and stress concentration at defects and notches. A single crystal of Ni-Mn-Ga was pre-strained in compression from 0 to 6% and then the shape was recovered with a magnetic field perpendicular to the loading direction while working against a pair of springs. The magnetic was raised from 0 to 0.64 MA/m and then reduced back to 0. Eight pairs of springs with combined spring constants ranging from 14.3 to 269.4 N/mm were used. When the magnetic field was on, the sample expanded against the springs due to magnetic field induce strain (MFIS). When the magnetic field was turned off, the springs compressed the sample back to the initial size before the next cycle. During each cycle, force and displacement were measured and the specific work was computed. Specific work increased with the applied magnetic field and the pre-strain. The maximum specific work was 14 kJ/m³ at a pre-strain of 4.5 % strain and a magnetic field of 0.64 MA/m.

FY 2014 HIGHLIGHTS

As demonstrated in previous studies, MSMA can sustain very large numbers of loading cycles. This study shows that stress concentrations associated with surface roughness, notches, SAGBs, and other defects substantially reduces fatigue life. Such defects represent obstacles to twin boundary motion. The interplay of moving twin boundaries with these defects leads to the accumulation of twinning dislocations which increase the local stresses and eventually cause crack nucleation. Cracks propagate preferentially along planes of high shear stress. The macroscopic fracture plans are typically close to

{111}. To achieve a long fatigue life, Ni-Mn-Ga crystals must be free of defects such as notches, small angle grain boundaries, and other sources of stress concentration. We showed that for an actuator with a spring-recovery, the maximum useful work output is only a small fraction of the theoretic limit given by the difference of work done by deforming the magnetic shape memory alloy with and without a magnetic field.

Mechanical Properties of Materials with Nanometer Scale Dimensions and Microstructures

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

We are engaged in a program of research on the mechanical properties of materials with micrometer and nanometer scale dimensions and microstructures. This includes work on both the mechanical properties of crystalline materials in small volumes and the emerging problem of mechanical properties of lithiated silicon for lithium-ion batteries. The research on small-scale plasticity focuses on understanding the dislocation processes responsible for the well known “smaller is stronger” effect on strength, which we, and others, discovered a few years ago, using the micropillar compression technique that we also introduced. Our work has included both experiments, using the micropillar compression technique, as well as computational modeling, using dislocation dynamics codes based on the ParaDis code developed at LLNL. The overall aim of the work is to determine the role that dislocations play in controlling the strength of crystals at small scales. Our experimental work has focused on determining the role of initial dislocation density on the mechanical properties in small-scale crystals through pre-straining experiments. Silicon has attracted great attention as a promising negative electrode material for lithium ion batteries due to its exceptional theoretical specific capacity of 3578 mAh/g. But the huge volume changes associated with lithiation and delithiation usually cause mechanical failure of the electrode to occur after just one charging/discharging cycle, unless silicon nanostructures are used. Our work on lithiated silicon has involved studies of the robustness of amorphous silicon nanostructures to resist fracture during lithiation and delithiation. We do this by studying the behavior of amorphous silicon micropillars after lithiation and delithiation and modeling the deformation and fracture behavior using finite element method (FEM) techniques. The aim of the work is to understand the factors that determine the critical size for failure of these nanostructures.

FY 2014 HIGHLIGHTS

We have developed a three-dimensional dislocation dynamics (DD) model to study the collective dislocation behavior in metal micropillars under compression, focusing on the role of dislocation sources at surfaces for both BCC and FCC metals. A few years ago Weinberger and Cai using molecular dynamics showed that dislocations in BCC micropillars can multiply by a surface-controlled cross-slip process involving image forces and non-planar core structures. We have created a DD model of that mechanism and used it to study the effects of micropillar size and microstructure on the strength of BCC micropillars. We have also used 3D DD simulations to study plastic deformation of submicron FCC micropillars with particular focus on the role of surface sources for these crystals. Based on atomistic

simulations, we have introduced an algorithm for dislocation nucleation at free surfaces as a function of stress and temperature in the DD code. Research on amorphous silicon nanoparticles shows that amorphous silicon is more fracture resistant than crystalline silicon during lithiation. But to fully exploit the potential of using amorphous silicon it is important to determine if larger, micron-sized, amorphous silicon structures can be lithiated without fracture. We have studied the morphologies of initially amorphous silicon micropillars up to several microns in diameter both before and after lithiation and have found no cohesive fracture, unlike crystalline Si nanopillars that fail for diameters greater than 300nm. Finite element modeling is used to understand the increased fracture resistance. Knowledge of the mechanical properties of electrochemically lithiated Si, needed for the FEM modeling, has been obtained using nanoindentation. We have studied both time-independent and time-dependent indentation of lithiated silicon and found that elastic modulus and hardness of lithiated silicon both decline markedly with increasing lithium content.

The Coupling Between Interfacial Charge and Mechanical Deformation at High Temperatures in Ceramics

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Funding: \$350,000 (2014-2015)

PROGRAM SCOPE

This BES program has led to the discovery of a new phenomenon, which has been called flash sintering, where oxide ceramics sinter in mere seconds at several hundred degrees below the temperatures for conventional sintering. The search for the underlying mechanism for this unusual effect is quickly leading to further findings. For example sintering is accompanied by a highly non-linear increase in conductivity, as well as intense photoemission. The rise in conductivity and photo-emission are observed in fully dense, pre-sintered specimens as well. Therefore, the flash event is intrinsic to the generation and mobility of charged and uncharged defects in ceramics. The neutral defects promote self-diffusion, while charged defects induce electrical conductivity. This coupling between charged and charge-neutral defects is vexing. We have proposed “nucleation” of Frenkel pairs that ionize into electrons and holes, providing conductivity and photoemission, and neutral defects that promote self-diffusion as a possible mechanism. This rather simple hypothesis has many assumptions and repercussions that are currently being investigated. In-situ experiments at Brookhaven (BNL) and Argonne (APS) Synchrotrons are beginning to provide insights into this phenomenon.

FY 2014 HIGHLIGHTS

There are two principal highlights during this calendar year. (I) Ultrafast sintering of oxides under an electric field, which has come to be known as flash sintering, has a fundamentally different mechanism of mass transport than the classical explanation where matter is transported from the grain boundaries to the pores by grain boundary or by lattice diffusion. We have shown, through experiments that have traditionally recognized the phenomenon of constrained sintering, that flash sintering likely occurs by the generation of Frenkel defects within the grain matrix, and that densification is accomplished by transporting the interstitials to the pores and the vacancies to the grain boundaries. (II) We continue to

make progress in in-situ experiments at the APS at Argonne National Laboratory. In these live experiments we measure the lattice expansion in the “flash state” and also search for new phases that form and vanish when the electrical field is turned on and off. The upper bound in the specimen temperature is measured by assuming that all the change in the lattice constant arises from thermal expansion. These temperatures are too low to account for the sintering rates achieved during flash sintering.

Mechanical Behavior in Ceramics with Unusual Thermal-Mechanical Properties

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Funding: \$155,000 (2014)

PROGRAM SCOPE

The study of materials with unusual properties offers new insight into structure-property relations as well as promise for the design of novel composites. In this spirit, the PIs seek to (1) understand fundamental mechanical phenomena in ceramics that exhibit pressure-induced phase transitions and negative coefficient of thermal expansion (CTE), and (2) explore the effect of these phenomena on the mechanical behavior of composites designed with such ceramics. The broad and long-term goal is to learn how to utilize these unusual behaviors to obtain extraordinary mechanical responses. While the results are expected to be widely applicable to many ceramics, most of the present focus is on silicates, as they exhibit remarkable diversity in structure and properties. Eucryptite, a lithium aluminum silicate (LiAlSiO_4), is specifically targeted because it exhibits a negative CTE and a pressure-induced phase transition at a sufficiently low pressure to be accessible during conventional materials processing. Thus, composites with eucryptite may be designed to exhibit a novel type of transformation toughening. The PIs perform *in situ* experiments and atomistic modeling to link structure and thermal mechanical behavior.

FY 2014 HIGHLIGHTS

In situ high pressure x-ray diffraction experiments have revealed that the high pressure phase of eucryptite belongs to an orthorhombic crystal system. Atomistic modeling was used to discover the mechanisms by which beta-eucryptite amorphizes under pressure or under irradiation and also the mechanism of radiation tolerance. Briefly, the material response to pressure or irradiation is to form alumina polyhedra along with the significant distortion of certain silica tetrahedra. Radiation tolerance is present because alumina polyhedra satisfy the oxygen coordination of distorted silica tetrahedra, thereby preventing the total collapse of the structure. It was found that tracking the oxygen coordination allows a description of amorphization and recovery.

NanoMechanics: Elasticity and Friction in Nano-Objects

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Funding: \$130,000 (2014)

PROGRAM SCOPE

Carbon is a fascinating element that takes highly diverse morphology and structure, from diamond to graphite, ending with interesting nano-forms like fullerenes, nanotubes and graphene. Nanotubes and graphene-based materials are well known for their exceptional thermal, mechanical and electrical properties, with the promise to become building blocks in integrated nano-electronic and photonic circuits, nano-sensors, electrodes in solar cells, hydrogen storage devices, nano-electro-mechanical systems, and in composite materials to improve the mechanical and electrical properties of ceramics and polymers. Here, we propose a research program to study the frictional properties and the radial deformation mechanisms of supported C- and BN- nanotubes (NTs) as a function of their morphology, e.g. radius, number of layers, and length; structure, e.g. chirality and defects; substrate interaction, and chemical functionalization. Furthermore, we plan to initiate a new research program on the mechanical properties of epitaxial graphene-based films on SiC and other 2D materials. The long-term goal is to understand, predict and manipulate the size, shape, chemistry and structure of C and BN based nanostructures, for producing nano-materials with tailored optimum mechanical, electro-mechanical and thermo-mechanical properties. The research activity will be divided in two parts: I. The frictional properties of individual NTs on a supported substrate will be investigated by atomic force microscopy (AFM). II. The out-of-plane elasticity of thin films of epitaxial graphene (EG) and epitaxial graphene oxide (EGO) grown on SiC, as well as other 2D materials will be investigated by performing Modulated NanoIndentation experiments by AFM as a function of chemistry, intercalates, number of layers, and substrate.

FY 2014 HIGHLIGHTS

1) We have discovered a method to produce exceptionally high quality graphene oxide thin films, based on the mild chemical oxidation of multilayer graphene films grown epitaxially on silicon carbide. By performing XRD and XPS studies, we discovered that multi-layer epitaxial graphene oxide (EGO) thin films have unique characteristics, making them ideal model systems to achieve fundamental understanding and control of both the oxidation process of sp^2 carbon and the relationship between mechanical and chemical properties of functionalized graphene. 2) Two-dimensional (2D) materials, such as graphene and MoS_2 , are a few-atomic-layer thick films with strong in-plane bonds and weak interactions between the layers. While their in-plane elasticity has been widely studied in bending experiments where a suspended film is largely deformed, very little is known about the elastic modulus perpendicular to the planes. Investigations of the out-of-plane elasticity require indenting supported 2D films less than their interlayer distance. Although experimentally challenging, studying the interlayer elastic coupling is critical, since it affects many properties of 2D films. Here, we report on sub-Å-resolution indentation measurements of the perpendicular-to-the-plane elasticity of 2D materials. Experiments, combined with semi-analytical models and density functional theory are then used to study the perpendicular elasticity of a few-layers thick graphene and graphene oxide films. Interestingly, we find that the perpendicular Young's modulus reaches a maximum when one complete water layer is intercalated between the graphitic planes. This non-destructive methodology can map interlayer coupling and intercalation in 2D films.

Using Artificial Microstructures to Measure Fracture Toughness in Metallic Glass and their Cellular Structures and Composites

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PROGRAM SCOPE

For most structural applications the materials' selection criterion is their resistance to fracture rather than its strength. The complex property of fracture toughness and its mechanistic origin is, however, not well understood for bulk metallic glasses (BMGs), which encompass alloys spanning from close to ideal brittle to remarkably tough behavior. The main reason for the limited fundamental understanding of fracture toughness of metallic glasses has been limited access to high and consistent quality test samples. To date, all fracture toughness test samples of BMG have been fabricated through direct casting which makes it challenging to fabricate consistent and high quality samples. To overcome these shortcomings, we propose an alternative fabrication approach based on artificial microstructures, developed during our previous funding period. Artificial microstructures are fabricated through thermoplastic forming, which drastically reduces problems such as porosity and stresses associated with casting of metallic glasses. Thermoplastic forming is unique among metals, and can be carried out for some BMGs with the ease similar to the processing of thermoplastics. Our goal is to use this method to fabricate >500 BMG fracture toughness test samples/year in order to perform a systematic and very broad study of fracture toughness of BMGs and their composites. Our study will provide an unprecedented quantity and quality of fracture toughness data on metallic glasses, which will be used by the metallic glass community to test and develop quantitative theories, and to potentially develop new metallic glasses that resist fracture better. In addition, the further development of the artificial microstructure method, and specifically its extension to 2⁺ materials, will allow the materials science and mechanics community to determine microstructure-property relationships for a broad range of complex microstructures.

FY 2014 HIGHLIGHTS

Flaws are inevitably present in engineering structural materials. In this project, we introduce a novel approach to study the flaw tolerance of bulk metallic glasses. Our approach allows us to systematically manipulate the notch radius which simulates the flaw size and investigate the influence of flaw size on the fracture resistance of BMGs. The accuracy, versatility, and reproducibility of our approach revealed that fracture toughness of BMGs decreases apparently with decreasing flaw size up to a critical value. Below this value fracture toughness is independent of flaw size, suggesting a flaw tolerance behavior of BMGs. Such flaw tolerance is surprising since bulk metallic glasses lack a microstructure which has been associated with flaw tolerance in other material classes. We explain such flaw tolerance by a critical stress controlled fracture where ρ_c is defined by the critical plastic zone. This zone defines a characteristic distance over which stable shear banding plastic process develops prior to fracture instability. The BMGs' specific characteristic distance varies widely which rationalizes the vast variety in their fracture behavior and suggest distinct flaw tolerance. Our finding is encouraging for BMGs'

structural applications since flaws smaller than ρ_c are increasingly difficult to avoid but are “indistinguishable” in their influence to the fracture toughness.

Deformed Materials: Towards a Theory of Materials Morphology Dynamics

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Funding: \$400,000 (2014-2015)

PROGRAM SCOPE

Practical mechanical materials are complex systems. They have ramified, often self-similar microstructure on a variety of scales, and they respond to mechanical forces and thermal annealing in an intermittent, bursty fashion. The principle investigator is using nonlinear shock-forming partial differential equations and ideas and methods from statistical physics to develop and analyze generic, prototype models for this emergent behavior. His group then uses these model systems to understand and explain the tangible, practical phenomena observed in mechanical materials. The investigator and his group are numerically probing model materials in ways designed to mimic their important experimental probes. They study macroscopic stress-strain measurements under anisotropic loading paths (Bauschinger effects). They study the resulting anisotropic microstructure evolution using correlation functions, scaling of misorientations and cell sizes, and fractal analyses. They study three different X-ray scattering methods: the 3DXRD far-field reconstruction of real-space evolution of the internal structure of microcrystals, Bragg peak-shapes and their analysis, and small-angle X-ray scattering probes of correlation functions. The investigator is expanding his methods to incorporate and explain new physical phenomena and materials properties. He is simulating the analogous evolution of structure in smectic liquid crystals with partial broken translational order (focal conic domains). He is developing new methods for extracting stress distributions in colloidal crystals from imaging analysis. By incorporating vacancies, solutes, and dirt he is studying the complex dynamics of climb and grain evolution, of the bursty Portevin-Le Chatelier (PLC) effect, of dislocation avalanches pinned by impurities, and of the investigator's newly discovered avalanche-oscillator route to criticality.

FY 2014 HIGHLIGHTS

The investigator's group has a spectacular new simulation of the evolution of focal conic domains in smectic liquid crystals. We use an effective theory and numerical simulations to study focal conic domains in smectic-A liquid crystals. In our simulations, focal conic structures spontaneously emerge from random initial configurations, and are characterized by several visualization tools that we developed. We describe the coarsening mechanism, and the scaling behavior of the probability distribution of the layer radii of curvature. We also study the effects of dilative and shear stress in this system, and compare the results with experiments from Itai Cohen's lab. These simulations lend deep insights into crystalline materials. By exploring broken translational symmetry in one dimension, we find new analogues to polycrystalline grains (focal conic domains), explanation of the 'frailty' of crystals (which form defects after tiny deformations compared to other systems), and provide a new testing ground for our simulation methods. The investigator has, in collaboration with Itai Cohen's group, developed a new method, 'Stress Assessment from Local Structural Anisotropy' (SALSA), for extracting

local stress information in colloidal crystals. Purely using the fluctuating positions of the colloidal particles, SALSA has allowed us to visualize the stresses around a dislocation, the nonlinear stresses around vacancies, and the residual stresses in a polycrystal – adding a whole new window into this model material system.

Radiation Response of Low Dimensional Carbon Systems

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Funding: \$450,000 (2014-2016)

PROGRAM SCOPE

The objective of this project is to understand radiation responses of low dimensional carbon systems and radiation-induced mechanical property changes at atomic scales. The materials to be studied include graphene monolayer, few-layer graphene, and carbon nanotube (CNT) bundles. In addition to studying effects from their different dimensions, sizes and geometries, the project will focus on boundary effects: (1) For graphene monolayer, the project will study defect sink properties of grain boundary, stimulated by modeling supported hypothesis that a grain boundary can trap defects for self repairing under ion/electron irradiation. Ion irradiation and *ex situ* transmission electron microscopy (TEM) characterization, and *in situ* TEM with concurrent electron irradiation, will be used to obtain atomic scale details of boundary-defect interaction on suspended graphene monolayer. (2) The project will study strained graphene monolayer to understand effects of strain on defect developments. Microfabricated tensile and compression test platforms will be used for *in situ* TEM characterization of graphene under stress and irradiation. (3) For few-layer graphene, the project will study the effect of inter-plane defects on graphene sliding. The proposed study will aid in fundamental understanding of the radiation responses of nanoscale materials. The knowledge will impact a wide range of carbon and non-carbon nanomaterials having a high surface to volume ratio, including nanomembranes, nanowires and fibers. Ion irradiation can either improve or degrade certain physical and chemical properties of carbon nanomaterials, and therefore this research is important to design and functionalize a wide range of nanomaterials-based structural components, microelectronics, sensors, and detectors.

FY 2014 HIGHLIGHTS

The major focus of year 2014 was to study boundary effects on radiation tolerance and structural changes of low dimensional carbon systems. We obtained the fundamental understanding on the geometry and quantum size effects on damage creation and defect annealing behaviors of ion irradiated carbon nanotubes and graphene. We reported large differences in carbon displacement creation under different tube configurations, and developed a multi-scale modeling approach to accurately calculate their displacement cross sections under different geometry and boundary conditions. Furthermore, both modeling and experiments suggested that migration energy barriers for defects on graphitic tube planes and for defects trapped between two touching tubes are largely different. Upon annealing, such difference leads to defect removal within tubes but creation of stable linking defects between tubes, which dramatically increase phonon transport in ion irradiated carbon nanotubes. For studies on graphene, we have shown that the energy barrier, which must be overcome to develop self-rolling, can

be lowered or completely eliminated by introducing vacancies. A structural transition diagram was created in which we show how ion irradiation of graphene can control curvatures of formed carbon nanoscrolls. Furthermore, using *in situ* electron irradiation and transmission electron microscopy, we studied the irradiation tolerance of few-layer graphene and reported easier structural collapse of the top and bottom layers of few-layer graphene, which is in good agreements with modeling prediction. Currently, we focused on the defect sink properties of grain boundaries in graphene under particle irradiation.

Understanding and Controlling Toughening Mechanisms in Nanotube Reinforced Ceramic Coatings

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PROGRAM SCOPE

The performance of ceramics is inherently limited by low fracture toughness, and it is well known that composite ceramic architectures can lead to significant toughness improvements. While long-fiber reinforcements can provide substantial advantages, basic length-scale effects do not necessarily point to substantial toughness improvements at the nanoscale. The DOE-BES research that we have conducted to date has made important advances in understanding the mechanisms that dictate toughness enhancements in carbon nanotube (CNT) reinforced ceramics. The primary objectives of the current work are to: (1) Understand failure and toughening mechanisms in ceramic matrices, reinforced with multiwall carbon nanotubes (MWCNTs). Much of this work focuses on information obtained from *in situ* mechanical testing – in particular, using nanoindentation of microcantilever beams at Brown and single CNT pull-out experiments at Rice University. (2) Determine the extent to which the critical properties governing toughness are coupled to one another in CNT-based materials - particularly the variations in fiber strength, the fiber-matrix sliding resistance, and the fiber-matrix debond energy (in conventional fiber-reinforced ceramics these quantities are generally viewed as independent properties). (3) Another component of this work is SWNT reinforced ceramics, where interwall sliding is no longer relevant, but where significantly different mechanisms may be able to impart toughness (i.e., initial evidence suggests that SWNTs inside of bundles can unfurl or uncoil).

FY 2014 HIGHLIGHTS

Interface coatings were applied to MWCNTs with atomic layer deposition (ALD), and these were incorporated in a polymer-derived ceramic (PDC) matrix. In general the ALD coatings increased pull-out lengths with high quality MWCNT's, whereas the same coatings reduced pull-out lengths when tubes with much higher defect densities were used. Additional insight into this unexpected behavior was obtained with in-situ single CNT pull-out experiments (carried out using a micro-fabricated device in a scanning electron microscope). This carefully designed study provides detailed information about interfacial interactions between CNTs and PDC matrices. The measurements show that 30 ALD cycles increase the interfacial shear strength (IFSS) of the CNT-PDC by 45%. This higher IFSS is believed to originate from the additional surface roughness, which leads to mechanical interlocking at the interface

during pull-out. The combination of high strength (low defect) CNT's and special surface structures obtained with carefully designed interlayers opens up opportunities for improving the mechanical properties of CNT-reinforced ceramic nanocomposites. Research with SWNT reinforced was also initiated during this period. Dense and homogenous CNTs-Al₂O₃ nanocomposites were successfully prepared through colloidal processing and spark plasma sintering. Indentation experiments show that MWCNTs are stronger in shear resistance than SWCNTs. MWCNTs with prior covalent functionalization are able to provide crack bridging in the corresponding Al₂O₃-matrix composites, while the same acid treatment is detrimental to the SWCNT mechanical properties. In-situ observation during crack propagation provides more direct evidence of the CNT bridging contributions in bearing the remarkable high applied load. The CNTs' sword-in-sheath failure also suggests intimate bonding between Al₂O₃ and CNTs which can provide effective load transfer from the matrix to the CNTs.

Dynamic Fracture in Dealloying Induced Stress Corrosion Cracking

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PROGRAM SCOPE

This research program examines the role of dynamic fracture processes in dealloying induced stress-corrosion cracking (SCC) of face-centered cubic alloys. This form of SCC is particularly relevant in energy conversion systems as many failures in alloys such as austenitic stainless steel can result directly from dealloying. Corrosion of such alloys often results in the formation of a brittle nanoporous layer, which we hypothesize serves to nucleate a crack that owing to dynamic effects penetrates into the undealloyed parent phase alloy for a distance of several microns. Since there is essentially a purely mechanical component of cracking, stress corrosion crack propagation rates can be significantly larger than that predicted from electrochemical parameters. Silver-gold alloys serve as a model system for this study since hydrogen effects can be neglected on a thermodynamic basis, which allows us to focus on a single cracking mechanism. There are two major types of experiments underway. One series of experiments is centered on dynamic fracture in monolithic nanoporous gold (NPG). High-speed 1,000,000 frame/second digital photography is used to measure crack velocity as a function of the porous length scale and electrochemical potential. The other set of experiments referred to as crack injection involves forming a porous dealloyed layer under controlled electrochemical potential and zero stress, removing the potential and subsequently loading the system. The results of these experiments are interrogated for cracking using the dual-beam focused ion beam/scanning electron microscope and aberration corrected scanning transmission electron microscopy (STEM).

FY 2014 HIGHLIGHTS

(1) Digital Image Correlation (DIC) was used to measure the Young's modulus and Poisson's ratio for monolithic 40 nm NPG. These numbers were used to determine the dilatational, shear and Rayleigh wave velocities. (2) Crack velocities were measured as a function of electrochemical potential and ranged from ~100 m/s at 0.5 V (NHE) to 200 m/s at 1.4 V (NHE). (3) Fracture toughness tests determined that the fracture toughness of 40 nm NPG was ~ 10 J/m². The dynamic fracture toughness was

determined by the elastic strain energy in the system, which was defined by the loading conditions. (4) STEM characterization of crack injection experiments in polycrystalline AgAu alloys revealed grain boundary porosity at the tip of arrested cracks. This porosity could be a result of either grain boundary dealloying or shock wave propagation. (5) Preliminary crack injection experiments performed on AgAu single crystals show injection to distances of order 2-5 microns.

Tunable Hetero-Epitaxial Shape Memory Alloys

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

Shape memory materials are used for a wide range of applications, from medicine to aerospace, due to the ability to recover their original shape after inelastic deformation and super-elasticity. The ability to engineer desired performance in these materials is of technological and basic-science importance and this project explores a novel avenue to achieve this using large-scale computer simulations. The goal of the team is to explore hetero-epitaxial integration develop composite shape memory meta-materials with improved or tunable properties. A successful project will provide a quantitative assessment of the potential and limitations of hetero-epitaxial integration as an avenue to develop shape memory materials with tailored properties. This may address some of the limitations that currently restrict the use of SMAs as active materials. From the point of view of basic science the effort will shed light into the fundamental phenomena that govern and limit the fabrication and performance of hetero-epitaxial SMAs nanostructures: i) coherency limits in terms of materials and size, and ii) the role of strain, interfaces, and free surfaces in their martensitic transformation and thermo-mechanical response. Shape memory materials have an enormous potential for a wide range of applications from nanoscale switches for communications and low power electronics to microfluidics and this project will contribute to the knowledge base necessary for the development of next-generation materials nanoengineered to achieve specific functionalities.

FY 2014 HIGHLIGHTS

During FY 2014 the team focused on atomistic simulations of temperature and stress-induced martensitic transformations in nano crystalline shape memory materials. They uses multi-million-atom molecular dynamics (MD) simulations with an embedded atom model potential parameterized for NiAl to provide an atomic picture of grain size effects on the martensitic transformation. They found that nucleation of the martensite phase occurs in the grain interiors due to the mechanical constraints of neighboring grains with different orientations. The martensite nuclei grow outwards up to the point that further transformation is hindered by the constraints imposed by neighboring grains. Decreasing grain size hinders the transformation process and the transformation is completely suppressed for samples with average grain sizes of 7.5 nm and less. This is consistent with experimental observations. Interestingly, mechanical loads can induce the martensitic transformation in samples with ultra-fine grains and, quite surprisingly, the sample with 7.5 nm grain size exhibits improved superelasticity as compared with its coarser grain counterparts. The simulations provide a picture of the processes that

govern the performance and fundamental limits of nanocrystalline shape memory alloys with atomistic resolution.

Interfacial Effects in Radiation Phenomena of Ceramics

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PROGRAM SCOPE

The overall goal of this project is to discover fundamental principles that control radiation effects in ceramics, as exemplified by silicon carbide, and to use this understanding to guide design of ceramics with superior radiation resistance. SiC is not only an archetypical covalent ceramic, but also it is a material of large technological interest for a wide range of nuclear energy and electronics applications. The focus of this project is to determine the role of buried interfaces in the recovery of radiation-induced damage. Increasing the volume fraction of surfaces and interfaces provides a highly promising path toward improving radiation resistance of materials, because interfaces act as sinks for radiation-induced defects. For instance, metallic systems with grain sizes refined to the nanometer regime have been shown to lead to significant enhancement of radiation tolerance due to the increased volume fraction of grain boundaries. Surprisingly, in many ceramics seemingly contradictory results have been reported regarding the effect of grain size refinement on radiation damage. These results show that in design of radiation tolerant materials it is critical to consider coupling of grain size to effects of other nano- and microstructural features. Our approach involves a close integration of multi-scale simulation methodologies (from quantum mechanical calculations to rate-theory models) with state-of-the-art experimental characterization techniques (such as high-resolution high-precision scanning transmission electron microscopy). Specific objectives of this project are to: (i) Unravel the effects of grain boundaries on defect evolution during irradiation; (ii) Discover the effects of radiation on grain boundary atomic structure and on grain boundary sink strength; and (iii) Identify stable configurations of complex defect clusters and their quantifiable contribution to radiation-induced phenomena in SiC.

FY 2014 HIGHLIGHTS

We have developed a genetic algorithm for optimization of defect structures embedded in a bulk crystalline material. Using a combination of this new algorithm and *ab initio* calculations, we determined the ground state structures of a number of small interstitial defects in SiC, “invisible” to traditional transmission electron microscopy (TEM). Understanding the structure and energetics of these defects is essential for development of predictive models for radiation-induced damage. We have also investigated mobility of small defect clusters in SiC using accelerated atomistic simulations based on the kinetic activation-relaxation technique and we predicted that defect clusters in SiC are immobile by thermal mechanisms up to 1200K. Surprisingly however, we have further discovered using high resolution scanning TEM that defect clusters can become mobile under electron irradiation. This is the first direct experimental observation of mobility of intrinsic defect clusters in a bulk material. We developed a model for radiation-induced diffusion, which predicts diffusion coefficients in excellent agreement with experimental values. These results fundamentally change how we view defect evolution

and damage annealing in ceramics because up to this point it has been typically assumed that clusters in these materials are immobile due to their high intrinsic energy barriers to migration. Finally, to understand evolution of radiation-induced damage and its dependence on the presence of grain boundaries, we used high resolution TEM to study radiation-induced amorphous domains in SiC. An unusual morphology of crystalline/amorphous boundaries was found, which was then identified as a result of the cascade overlap and reproduced by our multi-scale model. This mechanism of damage evolution is important for understanding grain size effects on irradiation damage as the grain size effects have been shown to depend on damage mechanisms.

EARLY CAREER: Linking the Codependence of Grain Boundary Structure and Density to Defect Evolution Mechanisms During Radiation Damage

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PROGRAM SCOPE

The aim of this project is to provide a fundamental understanding of how metallic nanocrystalline alloys can be utilized as radiation tolerant materials in future nuclear reactors. Information about the origin and mechanisms of damage at the nanoscale and how these mechanisms evolve as a function of grain boundary character (GBC) and density (i.e., grain size) is still unclear. Understanding and mitigating radiation damage is of paramount importance in the nuclear industry. Damage of structural materials is a major limitation to extended lifetime of current reactors, and implementation of future reactors. Information about the mechanisms of and evolution of damage at the nanoscale as a function of grain boundary structure and density (i.e., grain size) is still unclear. Further understanding of the kinetics of the following point defect behaviors is needed: the decrease in point defect density near the grain boundary, or denuded zone, and radiation induced segregation (RIS), the preferential diffusion of solute atoms near the grain boundary that result in chemical inhomogeneity at the boundary. *In situ* irradiation and analytical transmission electron microscopy techniques are being used to study both pure and alloy materials dynamically. Combined with analytical techniques such as STEM-EDS, EELS and APT, in-situ and ex-situ irradiation techniques are being used to study the effect of sink strength and density on defect clustering and behavior in relation to grain boundaries. This work is defining a framework for understanding the origin of radiation damage mechanisms in model BCC and FCC nanocrystalline materials, on which a foundation of radiation tolerant material development can be built. Key topics addressed by this work are (1) the influence of GB density and GB character (GBC) on damage accumulation in model nanocrystalline FCC and BCC alloys and (2) the effect of species dependent interstitial diffusion on the GB chemistry.

FY 2014 HIGHLIGHTS

Key findings include: (1) The determination that the role of grain boundary character in radiation induced defect sink strength is consistent from the mesoscale to nanocrystalline microstructures, as long as grain boundaries are equilibrium structures. (2) Precession electron diffraction can be used as a means of measuring dislocation density and emission, and also strain, during microstructural evolution.

(3) Grain boundary plane is a key factor in radiation induced segregation, however grain boundary saturation can and does occur. Since January 1, 2014: 1 paper published, 2 papers in review, 1 patent pending, 8 invited presentations, 7 student presentations at conferences.

Chemomechanics of Far-From-Equilibrium Interfaces (COFFEI)

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PROGRAM SCOPE

Brittle oxide functional materials, such as those utilized in solid oxide fuel cells and lithium batteries exhibit significant operational stresses induced via chemical and electrochemical diffusion across material interfaces. Virtually all battery storage materials undergo considerable mechanical strain during Li charging and discharging. Likewise, fuel cell components, operating under steep oxygen activity gradients, often suffer from chemically induced strains. The goals of this program are to develop models to predict chemomechanical phenomena in lithium battery and fuel cell electrodes and electrolytes, to characterize the relation between Li or oxygen nonstoichiometry and lattice dilation/contraction, to predict conditions for device failure related to rate dependent charge/discharge rates and develop a detailed understanding of the role of strain on transport within electrodes and electrolytes and on reaction rates related to electrochemical reduction and oxidation reactions occurring at the electrode/gas or electrode/electrolyte interfaces.

FY 2014 HIGHLIGHTS

A mesoscopic fully coupled electro-chemo-mechanical model was developed capable of accounting for the effects of Li diffusion and consequent isotropic or anisotropic volumetric expansion of the host materials. The numerical analysis simulates fracture within the electrode material and delamination at the interface between electrode particles and solid electrolyte. Crack formation and propagation is predicted by means of a cohesive zone model extended to include decreased Li flux across interfaces due to their loss of mechanical integrity. The effects of inelastic strain (i.e. dislocations) in altering the local defect equilibria, and the kinetics of transport and surface exchange in selected solid oxide fuel cell (SOFC) model materials (CeO_2 and SrTiO_3 -based), are now being examined. Static and dynamic atomistic modeling techniques are being employed to study the effects of edge dislocations on the stability and mobility of oxygen defects. At equilibrium, for ceria, trivalent cations and oxygen vacancies are found to simultaneously enrich or deplete either in the compressive or in the tensile strain fields around the dislocation. The associative interactions among the point defects in the enrichment zone, and the lack of oxygen vacancies in the depletion zone slow down oxide ion transport, a finding contrary to fast diffusion of atoms along the dislocations in metals, and should be considered when assessing the effects of strain on oxide ion conductivity. The first chemical and thermal expansion measurements of perovskite $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\alpha}$ SOFC electrodes were completed, enabling predictions of durability in working energy conversion and storage devices. Demonstrated strong coupling between thermal and chemical expansion behavior: thermal expansion depends on oxygen stoichiometry, and chemical expansion

depends on temperature. We experimentally confirmed our previous theoretical calculations demonstrating the important role of charge localization in controlling chemical expansion behavior.

Atomistic and Mesoscopic Study of Plastic Deformation of Alloys of Body-Centered-Cubic Transition Metals and Magnetic Iron

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PROGRAM SCOPE

The goal of this research is to provide a fundamental insight into the deformation and fracture mechanisms in body-centered-cubic (BCC) transition (refractory) metals. This is carried out by employing atomic level computer modeling of dislocations and other crystal defects. These metals and their alloys are the most important materials employed in the broad range of technologies involved in energy production and conversion. From the perspective of fundamental science, these metals have a mixed nearly free electron and covalent bonding, which leads to significant directional bonds. This presents a formidable scientific challenge for atomic level studies of extended defects and thus one of the principal tasks of this research is to take into account in atomistic calculations all the essential aspects of bonding. In transition metals the partially filled d-band invokes the dependence of the energy on bond angles and in the present research we are developing a new version of bond-order potentials (BOPs) that reflect well this bonding together with bonding mediated by nearly free s and p electrons. The BOPs are being developed for all non-magnetic transition BCC metals and further progress involves iron, in which ferromagnetism plays important role. As a further step is the development of these potentials for binary alloys. The link between bonding on atomic scale and the mechanical response of a material to loading is being established via a multiscale modeling. When investigating plastic behavior of BCC metals we concentrate on the structure and glide of 1/2 screw dislocations that control the plasticity of these metals. This is followed by the development of mesoscopic models of dislocation glide at finite temperatures the part of which is determination of the Peierls barrier employing the nudged-elastic band (NEB) method. The important novel concept is that the Peierls potential is a function of the full applied stress tensor.

FY 2014 HIGHLIGHTS

Numerical bond-order potentials (BOPs) were developed for non-magnetic transition metals V, Nb, Ta, Cr, Mo and W. The testing of these potentials has been made via comparison with calculations that were also carried out using a DFT method. These involve investigation of alternative higher energy structures, transformation paths connecting the BCC structure with other structures by continuously distorted configurations, evaluation of the vacancy formation energy and calculation of phonon spectra. In all cases the BOP calculations are in an excellent agreement with DFT calculations. This testing of BOPs clearly demonstrates that they are transferable to structures well outside the regime of the ideal BCC lattice and are suitable for investigating the atomic structure and behavior of extended crystal defects. Two novel aspects were discovered in this study. First, it was found that screening of the bond integrals that describe the covalent bonding mediated by the d electrons by neighboring s electrons is essential.

Only when the screening is included the dislocation studies lead to the dislocation glide that agrees with experimental observations. This demonstrates, for the first time, that the local electronic structure has to be fully accounted for when investigating dislocation behavior in transition metals. The second exciting finding is that when using the constructed BOPs the motion of the screw dislocation in Nb and V loaded in pure shear and/or tension is predicted to take place on the {101} plane with a Schmid factor much lower than that of the primary slip plane. This agrees with experimental observations in which such slip was found to dominate in both Nb and V. It was named anomalous and its origin is still not well understood. Our calculations suggest that it is likely that we are starting to understand its origin on the level of atomic bonding. This dislocation behavior is now studied in all transition metals.

Localized Deformation and Intergranular Fracture of Irradiated Alloys Under Extreme Environmental Conditions

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Funding: \$560,000 (2014-2015)

PROGRAM SCOPE

The local conditions for initiation of irradiation assisted stress corrosion cracking (IASCC) are the development of a high normal stress localized at the intersection of the dislocation channel (DC) and the grain boundary (GB), driven by the intense dislocation activity in the channels. By virtue of the strong bond between the oxide and the underlying metal alloy, the high stresses are relieved only by the rupture of the oxide film above the grain boundary, allowing contact between the high temperature water environment and the freshly exposed metal. A key feature of our approach has been the implementation of a mesoscale science approach that provided linkage from atomistic simulations of dislocation responses to the accommodation and emission of dislocations from grain boundaries, through direct observation of dislocations with irradiation defects and grain boundaries, to macroscale experiments. Having isolated these conditions, we are poised to address why this failure does not occur at every grain boundary that is favorably oriented, why it remains isolated at one channel over others along the same grain boundary, and what is the role of environment in inducing the cracking. With these questions in mind, our overall objective is to determine the basic processes by which localized deformation in irradiated materials leads to intergranular (IG) cracking in alloys in aggressive environments at high temperature. The program focuses on the following sub-objectives: (i) Since all DC-GB intersections do not result in cracking, what is the distinguishing factor or condition? If a threshold in stress for initiation of IASCC exists, can it be determined? (ii) Can the variability in cracking propensity between different alloys be explained by specific material properties such as stacking fault energy, grain boundary structure, or constraints imposed by the surrounding grains? (iii) What is the role that the water environment, either separately or in concert with a high localized stress state, in the cracking process?

FY 2014 HIGHLIGHTS

We have identified the various ways in which dislocation channels (DC) interact with grain boundaries and which are most likely to lead to nucleation of IASCC cracks. DC - grain boundary intersections are classified as either continuous in which slip is transferred across the boundary, discontinuous with grain boundary slip in which the slip is confined to the grain boundary plane, and discontinuous in which there is no evidence of transfer of slip to the neighboring grain or the grain boundary. Stress corrosion cracking tests in 288°C simulated boiling water reactor (BWR) water revealed that discontinuous channel-grain boundary intersections are several times more likely to result in IG crack initiation than either discontinuous channel interaction with grain boundary slip or with continuous channel – grain boundary interaction. Atomistic simulation studies of the interaction of dislocations with grain boundaries were performed in samples created with microstructures that mimic those studied in experiments. The simulations revealed that the arrival of a dislocation at the grain boundary is associated with increased stress. If the dislocations are not transferred across the boundary, crack formation is likely to develop as a result of the stress buildup. In the simulations 78% of cracks developed in boundaries with no slip continuity into the neighboring grain. The simulations also showed that slip transmission versus stress buildup at the boundary is affected by the grain boundary geometry, with 84% of the cracks developing in random high angle boundaries. The key finding at the mesoscale level was that the slip systems activated by the grain boundary in response to the accumulation of incident dislocations both at and in the grain boundary is determined by the same condition as in unirradiated materials. A distinct difference between unirradiated and irradiated austenitic stainless steels is that the magnitude of the locally resolved shear stress becomes important in the latter case.

Deformation Mechanisms of Nanotwinned Al

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Funding: \$150,000 (2014)

PROGRAM SCOPE

The objective of this program is to investigate at a fundamental level, the deformation mechanisms of nanotwinned (nt) Al films with high density growth twins and stacking faults (SFs). Growth twins have been introduced into certain fcc metals with low stacking fault energy (such as Cu, Ag and 330 stainless steels) to achieve high strength, high ductility, superior thermal stability and good electrical conductivity. However it remains a major challenge to produce growth twins and SFs in metals with ultra-high stacking fault energy (SFE), such as Al. Although deformation twins have been observed in nanocrystalline Al powders by low temperature, high strain rate cryomilling or in Al at the edge of crack tip or indentation (with the assistance of high stress intensity factor), these deformation techniques typically introduce twins sporadically and cannot control deformation twin density. This program is built upon our recent success of fabricating high quality epitaxial nt Al and will test the hypothesis that nt Al may have deformation mechanisms drastically different from those of coarse-grained Al and nt Cu. To test this hypothesis, we will perform the following tasks: (i) Investigate the stability of nanotwins and SFs in Al, (ii) examine if single crystal like nt Al has pop-in events during deformation, (iii) the interaction of dislocations with twin boundaries (TBs) in nt Al, (iv) mechanical stability of TBs and SFs in Al under

stress, and work hardening of nt Al. *In situ* nanoindentation will be used extensively to probe deformation mechanisms in nt Al.

FY 2014 HIGHLIGHTS

In this fiscal year, we have performed in-depth studies on three projects. (1) Investigate an intriguing twin formation mechanism in high stacking faulty energy metals We examined several sputter-deposited, {111} textured Ag/Al, Cu/Ni and Cu/Fe multilayers, wherein growth twins were observed in Al, Ni, and face-centered cubic (fcc) Fe. We derived two important criteria that enable the formation of twins in high SFE metals: (i) a low SFE buffer layer that readily forms twin seeds, and (ii) global coherency between coherent similar interfaces (between constituents with identical planar indices) or local coherency between coherent dissimilar interfaces (between constituents of different planar indices) that permits twins to propagate across layer interfaces. The formation of twin boundaries across layer interface could be a natural consequence of strain relaxation, in competition to the formation of misfit dislocations. (2) Establish a novel technique to reliably determine strain rate sensitivity of nanotwinned and nanocrystalline metal films. Nanoindentation is increasingly used to determine the strain rate sensitivity (SRS) of materials with small volumes. However traditional data analysis yields large scattering and uncertainty due to thermal drift at low strain rates. Here we use a new method that renders hardness insensitive to thermal drift. The method involves (a) directly measuring contact stiffness by means of a small dynamic oscillation and (b) calculating contact area from the measured contact stiffness and the elastic modulus, which is insensitive to strain rate. The new technique is validated on nanocrystalline Ni and nanotwinned Cu films and returns expected values of SRS. (3) We (Beyerlein, Zhang, Misra) wrote an review article (Ann. Rev. Mater. Res.) on growth twins and deformation twins. We anticipate that, by providing a broad perspective on the latest advances in twinning, this review will help set the stage for designing new metallic materials.

DOE National Laboratories

Nanomechanics and Nanometallurgy of Boundaries

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Funding: \$713,000 (2014)

PROGRAM SCOPE

Nanostructured metallic alloys have revealed intriguing scientific phenomena such as Hall-Petch breakdown and stress-induced grain growth, yet this class of metals is often plagued by grain structure instability, limited ductility, and a lack of available bulk processing routes. In the past 3 years, through 28 publications, this program has fostered a better understanding of grain boundary motion and grain growth as it relates to the unusual mechanical properties of nanostructured metals. While grain instability was once viewed as a detrimental attribute that was difficult to control and predict, our improved understanding of this phenomenon offers the opportunity to tailor stability for particular

thermomechanical environments. In the current year, we continue to explore the thermal, mechanical, and irradiation-induced stability of nanostructured interfaces. For this purpose, we rely on [1] thin film processing methods including pulsed laser deposition and magnetron sputtering to produce pure metals and binary nanostructured alloys of varying degrees of thermodynamically predicted stability, [2] *in situ* deformation, heating, and ion-irradiation of these films in the TEM, and [3] *ex situ* characterization before and after various mechanical environments (tension, shear, indentation, fatigue, wear). Molecular dynamics modeling continues to provide a complementary approach to addressing the questions regarding mechanisms governing boundary stability. The modeling and theory also provides a mechanistic foundation to assist in the interpretation of the experimental observations.

FY 2014 HIGHLIGHTS

In FY 2014, our focus was on quantifying the influence of special grain boundaries or chemically modified grain boundaries in processes associated with mechanically-induced grain growth. In our recent experiments, we have compared the indentation behavior of nanocrystalline and nanotwinned copper and found that sigma-3 (twin) boundaries facilitate extensive grain growth. Moreover, the grain growth is even more pronounced at cryogenic temperatures (4K and 77K) compared to room temperature, suggesting a potentially athermal mechanism. While other researchers have postulated that the twin boundaries facilitate grain growth through a 'de-twinning' process, our own non-local kinematic analysis of molecular dynamics simulations have shown a more complex superposition of several simultaneous mechanisms including twin nucleation and dislocation channeling as well as twin migration. These simulations also suggest that the relative contribution of the various mechanisms is different in tension versus compression. In addition to special boundaries that have unusual kinetic mobility, we have begun to investigate binary alloy combinations where segregation of the alloying element to the boundary provides a thermodynamic barrier to boundary migration. To this end, we have experimentally compared the thermal stability of nanocrystalline Fe-Mg and Fe-Cu alloys – two alloys that were previously predicted by Monte Carlo simulations to have marked differences in thermodynamic stability. Indeed the Fe-Mg alloy was profoundly more resistant to thermally-induced grain growth than the Fe-Cu alloy. Finally, this year we have collaborated with EMPA in Switzerland to perform resonant cantilever fatigue experiments that have provided an independent confirmation of our prior hypothesis suggesting that the grain growth process is a necessary precursor to crack initiation in nanocrystalline alloys.

Crack-Tip Mechanisms Driving Environmental Degradation

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Funding: \$631,000 (2014)

PROGRAM SCOPE

First-of-a-kind, discovery-based research is being conducted to explicate environmental degradation mechanisms through atomistic measurement and modeling of interfacial reactions occurring at buried crack tips. Degradation processes in corrosion-resistant alloys involve selective oxidation, vacancy injection and local composition changes along grain boundaries that cannot be adequately explained by existing theories. Revolutionary advancements in site-specific sample preparation, in-situ experimental methods and atomically-resolved 3D analytical tomography will be leveraged to develop a seminal understanding of underpinning mechanisms at the atomic scale that control the cracking response in high-temperature gaseous to lower-temperature aqueous environments. Definitive empirical observations will be correlated with innovative multiscale simulation tools to evaluate specific mechanisms that control degradation phenomena. Observations to date have revealed dramatic compositional and microstructural changes that accompany grain boundary selective oxidation. The rapid development of these features requires accelerated interfacial diffusion that can only be explained by oxidation-induced vacancy injection. Observed compositional redistributions ahead of oxidation fronts are consistent with predicted vacancy-mediated, grain boundary diffusivities for those elements calculated at the quantum mechanical level. Intergranular degradation is found to advance in many corrosion-resistant alloys by selective oxidation even at low temperatures. Observations are generally inconsistent with continuum mechanics and electrochemical model predictions underscoring the critical need for fundamental understanding at the atomic and molecular level. This program will define the mechanisms controlling environmental degradation through cutting-edge empirical observations and original modeling of grain boundary reaction processes that bridge from atomistic to macroscopic length scales.

FY 2014 HIGHLIGHTS

Selective oxidation of Cr in a Ni-Cr binary alloy is discovered to promote vacancy injection and an increase in grain boundary diffusion by more than two orders of magnitude during corrosion in hydrogenated water. Quantum density functional theory-based diffusivities of vacancies, alloying elements and interstitial oxygen in Ni grain boundaries have been determined to help explain vacancy enhanced Cr mobility in comparison to response for Al during selective oxidation. Grain boundary oxidation experiments in high-temperature gaseous environments have been performed on Ni-Cr and Ni-Al binary alloys enabling the first direct comparisons to intergranular (IG) corrosion/oxidation nanostructures produced in hydrogenated water. In-situ, high-resolution transmission electron microscopy (TEM) and energy dispersive x-ray spectroscopy revealed unprecedented nanoscale details of chemical partitioning caused by selective oxidation of Cr in a Ni-Cr alloy. The behavior of injected vacancies during oxidation was directly visualized leading to vacancy supersaturation, nucleation of a single cavity and subsequent sinking of excess vacancies. Quantitative measurements of IG stress corrosion and creep crack growth in high purity Ni alloys established that selective oxidation of Cr, Al and Si promoted environment-assisted cracking in comparison to response for pure Ni, Ni-Cu and Ni-Fe alloys. Unexpected enhancement in intergranular stress corrosion crack growth rates for high purity Ni-Cr alloys as bulk Cr concentration is increased from 5 to 20%, not consistent with observed grain boundary oxidation behavior. Initial development was completed on a multiscale simulation model that combines quantum density functional theory simulations of metal, oxygen, and vacancy diffusivities with an atomistic-to-mesoscale free energy based dynamics simulation of crack tip selective oxidation for comparisons with TEM and atom probe tomography measurements.

Multiscale Mechanical Properties and Alloy Design

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PROGRAM SCOPE

The overarching goal of this project is to advance fundamental understanding of mechanisms that control the mechanical behavior of crystalline metals across a broad spectrum of length scales. Of special interest are phenomena that cannot be explained by conventional theories. Examples include size-dependent mechanical properties and certain mechanical responses of compositionally complex (e.g., high-entropy) alloys that defy conventional notions of solid solubility. Our near-term focus continues to be on mechanical behavior at small scales approaching those of the fundamental processes responsible for deformation. We have also recently begun work on the mechanisms responsible for certain interesting mechanical responses of high-entropy alloys such as temperature dependent strength, large elongations, high work hardening rates, and the breakdown of the traditional inverse relationship between strength and ductility. Careful processing techniques are used to synthesize high-quality single- and poly-crystals with controlled microstructures and defect distributions. State-of-the-art microanalytical tools are then used to characterize their microstructure and mechanical behavior over the entire range of lengths scales from the nano/micro to macroscopic. Theory and modeling work aligned closely with the experimental effort are used to interpret the experimental results. The understanding gained as a result of this program will contribute to the development of broad scientific principles for the design of next-generation advanced structural materials.

FY 2014 HIGHLIGHTS

(1) A simple stochastic model to determine the pop-in load and maximum shear stress at pop-in, in nanoindentation experiments. J. Mater. Res. 28, 2728 (2013). The model incorporates pop-in due to nucleation of dislocations in dislocation-free regions, and pop-in by activation of preexisting dislocations. The model correctly predicts the experimentally observed average maximum shear stress at pop-in, and the scatter in pop-in loads and how it varies with indenter radius. (2) A high entropy alloy exhibits exceptional damage tolerance, with mechanical properties that improve at cryogenic temperatures. Science 345, 1153 (2014). High-entropy alloys are equiatomic, multi-element systems that can crystallize as a single phase. We found that the five-element high-entropy alloy, CrMnFeCoNi, has exceptional damage tolerance. Furthermore, its mechanical properties actually improve at cryogenic temperatures. (3) Recovery, recrystallization, grain growth and phase stability of a family of FCC-structured multi-component equiatomic solid solution alloys. Intermetallics 46, 131 (2014). All possible equiatomic subsystems of the high-entropy alloy FeNiCoCrMn were studied by assessing their available phase diagrams and experimentally verifying which of the sub-alloys formed single-phase FCC solid solutions. Neither the ability to form a single-phase solid solution, nor the degree of solid solution

hardening, was determined solely by the number of alloying elements; rather the type of elements present in the alloys needs to be taken into account. (4) Theoretical studies of Ir₅Th and Ir₅Ce nanoscale precipitates in Ir. Phil. Mag. 94, 991 (2014). Very small amounts of thorium or cerium added to iridium metal improve the high-temperature mechanical properties of the resulting alloys. We demonstrate that there are low-energy configurations for nanoscale precipitates in Ir, and that these coherent arrangements may assist in producing improved mechanical properties.

Evolution of Grain Boundary Networks in Extreme Radiation Environments

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PROGRAM SCOPE

Advanced nuclear energy systems will require materials to perform for long periods in elevated temperatures and high radiation conditions. Conventional materials lack the required microstructural stability in such environments. Grain boundaries (GB) in nanocrystalline materials can substantially mitigate this degradation by acting as highly effective sinks for point defects. Unfortunately, such materials can be thermally unstable, thus reducing their long-term efficacy. Our previous work shows that GB networks consisting of a high fraction of annealing twins and related boundaries can be stabilized against thermal coarsening. We are studying whether such GB networks can also enhance microstructural stability under irradiation. The proposed work aims to address the overarching question: What must a GB network look like if it is to act as an effective point defect sink, not only on initial deployment, but after years of severe irradiation? We envision a network in which high free volume “random” boundaries act as point defect sinks while the more stable special boundaries anchor the network, and the entire ensemble is statistically stable over long periods. We have successfully elucidated the thermal annealing characteristics of nanostructured copper, relating the relative coarsening rates for various microstructural morphologies to the nature of the quadruple nodes in the GB network. We have also elucidated the role of the GB network on radiation-induced GB migration, particularly for nanotwinned copper. These observations are being augmented by 3-D HEDM observations on conventional microstructures, which provide an unprecedented window into the correlated nature of GB networks and its effect on coarsening behavior. These results are also being corroborated through Monte Carlo (MC) simulations of coarsening behavior. These simulations are being informed by a newly constructed function that universally treats GB energy anisotropy for all FCC materials.

FY 2014 HIGHLIGHTS

Conducted a study that resulted in a major modification to how Monte Carlo methods are used to simulate microstructural evolution. Used our newly developed energy function for grain boundaries to document the change in total energy of the system during microstructural evolution. In-situ high energy electron irradiation was used to investigate how grain boundary networks influence radiation-induced boundary migration.

Nanotwinned Materials for Energy Technologies

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PROGRAM SCOPE

Nanotwinned metals and alloys are emerging as a particular form of nanoscaled material that can exhibit high strength coupled with improved thermal stability, both of which are yet unexplained. We have developed an integrated experimental, modeling and simulation program to examine the underlying mechanisms of plasticity in nanotwinned samples. We employ a range of methods to create systems with differing twin morphologies and microstructures and characterize their structures using a range of techniques, from electron microscopy to synchrotron scattering to the use of an atom probe. Mechanical testing of these samples is carried out in a novel tensile strain stage that enables accurate measurements of stress-strain behavior with concurrent *in situ* transmission electron microscopy (TEM) observations of evolving microstructures. We will also use a temperature-controlled nanoindenter to characterize the thermal dependence of the mechanical properties. The experiments are coupled with a modeling and simulation program that includes atomistics, dislocation dynamics and polycrystal plasticity simulations. The experiments provide both realistic validation of models and a deeper understanding of fundamental mechanisms, enhancing the development of new understandings of deformation in nanotwinned materials. This program will not only shed new light on plasticity in nanotwinned materials by bridging the current gap between the experiments and modeling, but it will also greatly enhance our overall understanding of many collective and cooperative mechanisms of plasticity in these materials.

FY 2014 HIGHLIGHTS

In FY 2014, experimental and theoretical studies were performed to examine the effects of solute on the strength and thermal stability of nanotwinned materials. Our experimental studies on nanotwinned silver showed a large strengthening effect from copper additions. Molecular dynamics simulations of twin boundary migration in the presence of impurities showed a considerable impurity drag effect that cannot be described by classical solute-drag models.

Stability of Nanoclusters in Metal Matrices under Extreme Environments

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Funding: \$928,000 (2014)

PROGRAM SCOPE

The goal of this project is to understand the formation mechanism, energetics, and fundamental hardening behavior associated with stable nanoclusters in metallic alloys and to establish a fundamental understanding of the mechanisms that control their response to intense irradiation and other extremes. The specific aims of the proposed research are to establish the mechanisms for homogenous and heterogeneous nucleation that occur during the earliest stages of formation of nanoclusters and helium bubbles in materials far from equilibrium, to understand the mechanisms that enable radiation tolerant behavior to be achieved in structural steels that are exposed to high doses of irradiation, and to understand the interaction of dislocations with the nanoclusters and other microstructural features in an ultra-fine grain nanostructured ferritic alloy, and hence understand their remarkable mechanical properties. The mechanisms will be elucidated through a synergistic approach of *ab initio* theory, computer simulation and modeling and atomic level experimental characterization of nanostructured materials before and after neutron and ion irradiation by atom probe tomography, analytical and scanning transmission electron microscopy ((S)TEM), weak-beam TEM, novel high-resolution TEM techniques with near atomic resolution of dislocation cores, and neutron scattering. This basic research is ultimately aimed at developing the understanding needed to enable fundamental discoveries regarding nucleation and defect mechanisms in nanostructured materials. The scientific principles developed with this research are expected to have a broad applicability in the synthesis of new-generation nanostructured materials with high-temperature capability for use in advanced energy production and conversion systems under extreme environments.

FY 2014 HIGHLIGHTS

The size and number densities of solute clusters in the ferrite of as-milled mechanically alloyed nanostructured ferritic alloy (NFA) and the stir zone of a friction stir weld were estimated with a prototype high-detection-efficiency LEAP. Solute clusters containing between 2 and 9 Ti, Y and O atoms were detected, providing addition trapping sites for vacancies. Different types of nm-scale precipitates in NFA were identified by combined aberration-corrected electron microscopy and high-efficiency X-ray chemical mapping. By combining advanced STEM hardware with detailed computational datamining of X-ray chemical maps, subtle details of the irradiation effects were identified, such as chemical segregation to grain boundaries blurred by ballistic mixing under cryoirradiation. The distribution of He bubbles at grain boundaries, on nanoclusters, or in the matrix of irradiated NFA has been elucidated by new aberration-corrected electron microscopy methods. Operating the microscope to achieve Fresnel contrast in STEM mode, combined with Z-contrast imaging and elemental mapping, made it possible to detect the smallest ~ 2 nm He bubbles. A thermodynamic DFT-based approach has been developed to estimate the thermodynamic equilibrium by the minimization the free energy of the whole multiphase system with respect to defect production. It uses a limited number of defects and microstructural objects, which properties are calculated from first-principles, allowing the global stability to be studied as a function of composition, internal microstructure, temperature, externally produced defects, etc. Our results confirmed the high temperature stability of Y_2O_3 in Fe. *In situ* neutron diffraction of orientation-dependent lattice strains in ferrite grains reveals a large, temperature-sensitive elastic

anisotropy and a deformation crossover on extensive straining. The novel approach provides a new strategy for characterizing anisotropic elasticity of a variety of complex materials.

Mechanical Behavior of Materials

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PROGRAM SCOPE

The attainment of strength and toughness is a vital requirement for structural materials; unfortunately these properties are generally mutually exclusive. It is the lower strength, and hence tougher, materials that find use for most safety-critical applications where premature, or worse still catastrophic, fracture is unacceptable. Accordingly, the development of strong and tough materials has traditionally been a compromise between hardness vs. ductility. The aim of this program is thus to seek the scientific strategies to solve this “conflict” by defining the basic scientific principles underlying the development of damage-tolerance in lightweight structural materials suitable for the strategic missions of energy and conservation/creation. One approach involves the understanding of the scientific origins of damage-tolerance in new advanced metallic alloys, principally bulk-metallic glasses and high-entropy alloys, where the salient mechanisms involve a balance of intrinsic vs. extrinsic toughening. A second approach involves using concepts of natural hierarchical design to examine the interfaces between the physical and biological sciences in the development of biomimetic hybrid ceramics. Our hypothesis here is that by mimicking natural structural architectures and identifying and incorporating the salient strengthening and toughening mechanisms at multiple length-scales, guided by theoretical modeling at atomistic to continuum levels, and coupled with the use of novel processing techniques, we can develop the scientific foundations for unique lightweight biomimetic structural ceramics materials with unprecedented levels of damage-tolerance. In all cases, our focus is on the scientific interplay between the individual nano/micro-mechanisms that contribute to strength and toughness, that of plasticity and crack-tip shielding, noting that these phenomena originate at very different structural length-scales.

FY 2014 HIGHLIGHTS

A new alloy design concept, high-entropy alloys, has been found to yield a material with exceptional cryogenic fracture toughness properties. Unlike most materials, this alloy shows increasing strength, ductility and toughness with decreasing temperature, associated with the onset of deformation by nanoscale twinning at low temperatures. (Gludovatz *et al.*, Science 2014). Additionally, a novel computational modeling approach has been established to predict the statistical failure of Nature-inspired ceramics at multiple length-scales. Material properties can be created at specific microstructural levels, but must be designed with regard to their macroscopic distribution. Our model permits the physically-based coupling of micro-scale criteria to macroscopic behavior, bridging the micro- and macro-scales. (Genet *et al.*, J. Mech. Phys. Sol., 2014).

Multi-Scale Study of the Role of Microstructure in the Deformation Behavior of Hexagonal Material

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PROGRAM SCOPE

Dislocation glide on atomic planes is the most common shear accommodation mechanism in crystals. However, in Hexagonal Close Packed (HCP) materials and some austenitic steels dislocation glide is restricted and shear is simultaneously accommodated by twinning and martensitic transformations, respectively. These transformations require a previous nucleation process governed by stochastic rules, and they propagate by shearing a domain of the grain where a crystal transformation takes place. In this Program we have performed a comprehensive study of the shear mechanisms of twinning in HCP and started studying martensitic transformations in Transformation Induced Plasticity (TRIP) steel. We link these transformations with the macroscopic plastic response of metallic aggregates. The systems studied are the HCP metals Mg, Zr, Be and TRIP steel 304STS and 301LN. This comprehensive research links modeling with experimental studies, at length scales spanning from the atomistic to the continuum. The overarching goals are: a) to improve our understanding of the basic crystallographic mechanisms of shear localization and their role in deformation; b) to develop a predictive multi-scale modeling capability based on such mechanisms. The deliverables of this project are: state-of-the-art material models at atomistic (micro), grain (meso), and polycrystalline (macro) length scales; mechanism-based constitutive laws for HCP and TRIP; new experimental characterization techniques.

FY 2014 HIGHLIGHTS

(1) Used MD, DFT and TEM to further the understanding of Basal-Prismatic (BP) segments in Coherent Twin boundaries (CTB) in HCP. We believe that these segments play a key role in twin mobility. We uncovered atomistic and dislocation mechanisms through which these segments propagate. We performed a comprehensive DFT study of alloying element interaction with BP segments and with CTBs, as preliminary stage to elucidate the role of alloying elements in twin mobility. (2) Uncovered the predominance of atomic shuffle mechanisms (as opposed to twinning dislocations) in the initial stages of twin nucleation and in twin propagation under special boundary conditions. (3) Developed a Crystal Plasticity model for simulating stress induced martensitic transformations in TRIP steel and combined it with measurements of in-situ neutron diffraction to understand the driving forces behind martensitic variant selection during TRIP steel deformation. (4) Developed a stochastic model of stress relaxation, based on distributions of dislocations segments and distributions of internal stress in grains. Implemented this statistical approach in our Elasto-Plastic Polycrystal model (EVPSC). This development provides a way to interpret results of in-situ neutron diffraction experiments. The experiments were done on Mg AZ31 alloy.

The Relationship Between Defect Kinetics and Crystalline Disorder

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PROGRAM SCOPE

Mass transport is the defining property for a number of technologically important complex oxides, with numerous applications, from fuel cells to nuclear materials. Thus, there is great incentive for both predicting and controlling mass transport. While there are multiple approaches for controlling diffusion in complex oxides, from doping to microstructure, intrinsic site disorder, in which cation species of different types exchange position, is a key mechanism for controlling transport that has been largely untapped. We argue that there is great untapped potential in both predicting and controlling diffusion as it relates to site disorder in complex oxides. Regarding prediction, given that site disorder greatly influences radiation damage evolution in complex oxides, there is a need for understanding not only anion but also cation transport and how both depend on site disorder in the material and how that site disorder depends on crystal structure and chemistry. Conversely, radiation damage can be used as a tool to control site disorder in complex oxides. We use a combination of state-of-the-art atomistic modeling methods with advanced experimental characterization to determine how the atomic scale mechanisms governing mass transport depend on the local site disorder as a function of the chemistry and structure of the material. In particular, we combine atomistic modeling, both molecular dynamics and accelerated molecular dynamics, with thin film growth and characterization to determine how site disorder controls mass transport, with an initial focus on anion diffusion. We examine both the unit mechanisms responsible for diffusion as well as the aggregate behavior within the sample.

FY 2014 HIGHLIGHTS

(1) Using accelerated molecular dynamics methods, we examined the mobility of oxygen vacancies in a series of complex oxides. We examined the pathways in terms of a layered stacking motif, which provided novel insight into how the structure of the oxide determines the mobility of oxygen vacancies. Finally, a kinetic Monte Carlo model was developed to study the impact of different pathways on the overall diffusion of oxygen. These results provide new insight into how crystal structure and chemistry influence defect mobility, important for both energy applications such as fast ion conductors as well as predicting radiation damage evolution. (2) Using a combination of atomistic simulations (density functional theory and molecular dynamics), we found that the formation energy of antisite defects in pyrochlore, a key quantity for predicting radiation tolerance in pyrochlore, depends on antisite separation. Collision cascade simulations show that the separation depends on irradiation conditions. Together, these results suggest that the radiation tolerance of titanate pyrochlores, as opposed to other pyrochlores, will be very sensitive to irradiation conditions and could be controlled. (3) In collaboration with X. Zhang at Texas A&M, we examined radiation damage evolution in ZnO nanowires. We used rate theory modeling, informed by atomistic calculations, to interpret the experimental results on the size distribution of dislocation loops in the wires as a function of wire diameter. Using the modeling allowed

us to identify the rate-limiting step for interstitial diffusion, which we found to be about 0.3 eV, which allowed us to discriminate between various literature values. (4) In collaboration with C. Jiang at Thermocalc, we have developed a new approach to studying chemically complex materials computationally. It allows for high-throughput calculations for materials with large numbers of species, such as high entropy alloys (HEAs) or chemical complex oxides.

Deformation Physics of Ultrafine Scale Materials

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PROGRAM SCOPE

This program investigates the deformation physics of ultra-fine scale materials with strengths near the theoretical limits. The descriptions of the mechanisms that determine the strengths and failure limits of such materials lie within new, largely unexplored or unconventional, realms of behavior. Currently, the program is focused on metal-ceramic nanolaminates. The key objectives are to explore: (1) room temperature plasticity, at unusually high strength levels, in nanoscale ceramics afforded by co-deformation with a metal, and (2) mechanisms that enable stable crack growth in nanoscale metal-ceramic nanolaminates. We apply a highly synergistic combination of state-of-the-art atomistic modeling and cutting-edge experimental methods that are able to probe the same nanoscale dimensional features. Specifically, the integrated approach consists of synthesis of nanolayered materials primarily via physical vapor deposition; *in situ* characterization of nanomechanical behavior via scanning and transmission electron microscopy; first principles calculations of interface properties and dislocation-interface interactions; development of empirical interatomic potentials for the metal-ceramic systems to be studied; and molecular dynamics and dislocation dynamics simulations of strain hardening and crack propagation; crystal plasticity modeling of the stress-strain response. This program focuses on developing understanding of the deformation and fracture behavior of materials near their theoretical strength estimates of perfect crystals, and should catalyze new advances in the applications of such materials. The applicability of this knowledge should impact a broad range of engineering materials, such as load-bearing structural components, advanced nuclear energy systems and electro-mechanical systems. It seeks to inspire the development of new materials with attractive combinations of mechanical, electrical, and thermal properties.

FY 2014 HIGHLIGHTS

(1) We proposed and demonstrated “Interface-assisted ductility in “brittle” materials” where materials are brittle and less dislocation activity at room temperature, such as ceramics. Using our developed Three Dimensional Crystal Elastic-Plastic Model (3DCEP), we ascribe the high strain hardening rate to the closely spaced dislocation arrays deposited at interfaces and the load transfer as related to the layer thickness ratio of metal and ceramic layers. We also developed a map that predicts plasticity in nano-

ceramic layers as a function of the ceramic layer thickness and the interfacial dislocation content. (2) We proposed a concept “Interface-enhanced toughening in high-strength nanostructured materials” and performed preliminary study by combining *in situ* SEM bending testing and multi-scale modeling. (3) We explored dislocation activity in ceramics (TiN) using DFT and *in situ* indentation in a TEM. The resistance to glide of lattice dislocations is a fundamental property that determines the deformation and fracture behavior of ceramics. For the first time, using density functional theory (DFT), the lattice resistance to glide (Peierls stress) has been computed for the viable slip systems in TiN. The DFT results will enable the design of metal-ceramic composites where ceramics can plastically co-deform with the metal at unprecedented strength levels. DFT simulations have been carried out to study the preferred slip systems and their respective Peierls barriers in TiN. Using *in situ* indentation in a TEM, we for the first time probed slip systems, critical resolved shear stresses for nucleation and glide of a lattice dislocation in TiN. (4) We further develop the method of interface defect characterization, Atomistically informed Frank-Bilby (AIFB) theory, to characterize interface defect structures and dislocation activity at interfaces. This method can be applied for any crystalline materials.

Electronic and Atomic Response of Ceramic Structures to Irradiation

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PROGRAM SCOPE

The overarching goal of this research is to understand, predictively model, and ultimately control the dynamic response of ceramic structures to irradiation at the level of electrons and atoms. The design of radiation tolerant materials and creation of new functional materials by ion beam modification demand a comprehensive understanding and predictive models of energy transfer and exchange processes at the level of electrons and atoms. To achieve this goal, this research will focus on two specific aims: (1) the dynamic and coupled response of electronic and atomic structures to single ion events; and (2) the collective effects from the coupled dynamics of electronic and atomic processes on damage accumulation, phase transformations and recovery processes for multiple ion events over a broad range of conditions. Novel experimental techniques and multi-scale computational approaches are integrated to investigate the separate and coupled dynamics of electronic and atomic processes over a range of irradiation conditions to elucidate the underlying mechanisms. This research will leverage unique experimental capabilities for measuring *in situ* the response of ceramics to ion irradiation and to individual single ion events, as well as the unique materials synthesis, characterization and modeling resources at Oak Ridge National Laboratory. The scientific advances from the work will not only lead to the design of self-healing and radiation tolerant materials for advance nuclear energy systems, but will provide the foundation for the design and control of material properties that enable broad advances in sustainable energy technologies and national security.

FY 2014 HIGHLIGHTS

We have demonstrated that the energy transferred to electrons by energetic ions via inelastic ionization processes results in a highly localized thermal spike that can effectively heal pre-existing defects and restore the structural order in SiC over a broad range of energies. This self-healing process provides a unique approach for improving SiC based devices, could extend the performance lifetime of SiC in fission and fusion reactor environments, and has significant implications regarding the use of high-energy ion beams and accelerator-based neutron sources for predicting the response of SiC and other materials to fast neutrons. We have discovered that a colossal synergy occurs between inelastic energy loss by ions and pre-existing atomic defects in single crystal SrTiO₃, resulting in the formation of nanometer-sized amorphous tracks. This work identifies a major gap in understanding on the role of defects in electronic energy dissipation and electron-phonon coupling and provides insights for creating novel interfaces and nanostructures to functionalize thin film structures with tunable electronic, ionic, magnetic and optical properties. Density functional theory has been used to predict that the Schottky defect complex is the most stable defect structure in stoichiometric SrTiO₃. Excess SrO leads to the formation of oxygen vacancies and cation antisite defects; excess TiO₂ leads to strontium vacancies, oxygen vacancies and cation antisite defects. These defects play critical roles in controlling the functionality of SrTiO₃. Density functional theory has been used to determine the formation and migration energies of neutral and charged oxygen defects in cubic zirconia. Positively charged oxygen vacancies and negatively charged split-interstitials are the most stable defects. The energy barrier for diffusion of the positively charged oxygen vacancy is significantly less than for the neutral vacancy.

Neutron Scattering

Institutions Receiving Grants

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Funding: \$1,400,000 (2014)

PROGRAM SCOPE

While quantum mechanics is normally associated with electronic motion at the atomic scale, it also finds expression in exotic materials properties. Understanding and controlling “quantum materials” presents one of the grand challenges at the intellectual frontier of the 21st century physical sciences and holds the potential for applications with transformative impact on energy and information technologies. Assembled to advance quantum materials, six PIs with expertise in materials synthesis, neutron and photon spectroscopy and theory form the Institute for Quantum Matter. In a close collaboration coordinated by project director Collin Broholm, they explore quantum materials in the following categories: Frustrated Quantum Magnets where quantum fluctuations supplant conventional static magnetism by a magnetic quantum fluid with exotic particle-like excitations. Examples of quantum magnets to be synthesized in pure crystalline forms and analyzed through spectroscopy and theory include molecule-based magnets, fluoride pyrochlores, and Ising spin chains. Topological Materials where the geometrical character of the bulk stabilizes exotic electronic surface states. IQM shall explore topological Kondo insulators, Weyl-semi metals, and topological superconductors. Correlated Metals: Magnetism near the metal insulator transition will be examined in heavy fermion and organic metals. At the quantum critical point where magnetism collapses, there is a potential for anomalously high temperature superconductivity. Empowered by national facilities such as SNS at ORNL and the NIST center for neutron research, the coordination of key expertise in synthesis, advanced characterization, and theory within IQM seeks to discover and understand quantum materials that can fuel technological progress and meet pressing societal needs.

FY 2014 HIGHLIGHTS

The theory of quantum spin liquids was advanced by identifying quasi-particles in tractable theoretical models of interacting spins with the potential for realization in materials. A new type of frustrated magnets based on fluorine as anion was discovered and synthesized in single crystalline form and subjected to neutron scattering. THz photon spectroscopy was shown to be highly effective for probing anisotropic frustrated systems including quantum spin ice, a quantum spin-orbital liquids, and anisotropic quantum spin chains. A molecular based frustrated magnetic material $\text{LiZn}_2\text{Mo}_3\text{O}_8$ was

developed and subjected to an array of experiments. The material exemplifies entangled magnetism based on static or dynamic singlet formation. Raman experiments that reveal quenched disorder and numerical theoretical work was applied to understand the short range correlated nature of magnetism in the spin-1 triangular lattice antiferromagnet NiGa_2S_4 . Raman scattering was also used to reveal two magnon excitations in the ordered organic magnet $\kappa\text{-(BEDT-TTF)}_2\text{Cu[N(CN)}_2\text{]Cl}$. Neutron scattering and THz photon spectroscopy was carried out on a number of strongly correlated metallic systems to understand the quantum critical point where magnetism collapses. Neutron scattering and theoretical work advanced our understanding of topological Kondo insulators and Weyl semimetals including SbB_6 , CeRu_4Sn_6 , and $\text{Pr}_2\text{Ir}_2\text{O}_7$. Theoretical work was carried out to understand anomalous conductivity by surface modes in Weyl semimetals. A neutron scattering study of magnetic excitations in BaFe_2Se_3 showed the importance of square blocks of four iron atoms in a class of materials that hosts iron superconductivity. A new method for growing crystals from the melt within an optical image furnace was developed and demonstrated in the IQM crystal growth lab. This scientific work at IQM was described in more than 20 publications and more than 50 invited talks.

Application of *In Situ* Neutron Diffraction to Understand the Mechanism of Phase Transitions During Electrochemical Cycling of High Capacity Mg/Si Nanostructured Electrodes

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Sr. Investigator(s):
Students: 0 Postdoctoral Fellow(s), 2 Graduate(s), 1 Undergraduate(s)
Funding: \$116,592 (2014)

PROGRAM SCOPE

The primary objective of this research is to perform *in situ* neutron diffraction experiments under electrochemical conditions to understand the fundamental nature of phase transitions during Li insertion/extraction in Mg/Si nanostructured high capacity electrodes. A novel electrochemical cell, that enables time-averaged *in situ* observations of bulk phase transitions, will be constructed and optimized for this research. The cell will be used to understand the phase transitions in electrodes made with different nanoparticle sizes and embedded in a conductive medium. The key objective is to discover the particle sizes and compositions at which electrochemically reversible transformations would occur. Mg/Si nanomaterials are the most suited for this study because they (i) can provide very high energy-storage capacity, (ii) offer many phase transition paths representing most anode materials and (iii) present the greatest challenge in anode material science. In particular, the research will investigate (i) how the changes in particle size and composition of the electrodes affect/limit the phase transitions and cell degradation and (ii) how the potential windows and rate of charge/discharge rates affect the kinetics of phase transitions and (iii) the kinetics of formation of the solid electrolyte interface (SEI) layer in the electrode-electrolyte interface. The research will be performed in collaboration with SNS facility at Oak Ridge National Laboratory where the *in situ* neutron diffraction experiments will be conducted. The understanding of phase transitions in Mg/Si electrodes can lead to breakthroughs in electrode chemistry and design for high energy-storage capacity Li-Mg and Li-Si cells. The research can have a large impact in battery materials science. The lack of reversible phase transformations in electrodes based on these materials, over a large number of cycles, has been the bottleneck that is preventing the realization of high capacity battery systems.

FY 2014 HIGHLIGHTS

Our neutron diffraction (ND) work revealed the transient nature of phase transformation in Li-ion batteries; the key finding is that the multiple lithiated phases, for example, Li_xC_6 , LiC_{12} , LiC_6 , co-existed/overlapped in the bulk of the electrode during the major period of charging of the Li-ion cell. Such finding has not been made in X-ray diffraction (XRD) work. Lithiation proceeded by the consumption of the Li-lean phase by the Li-rich phase. This shows that the phenomenon is akin to equilibrium solid-state phase transformation. This also provided indirect evidence that phase transition occurs by planar front movement, raising questions about the porous electrode theory, which is commonly believed. The ND data was obtained in real time and simultaneously on both anode and cathode, which has not been possible with XRD. This way, our work enabled direct one-to-one correlation of phase transitions in anode and cathode and allowed us to directly identify which electrode is limiting the charge capacity of the cell. In particular, we found out that for the LiMnO_2 electrode, the electrode thickness needs to be increased to fully transform C to LiC_6 . Such simultaneous ND diffraction provides a clear illustration of importance of optimizing electrode thickness, especially keeping mind the full phase transformation path. The *in situ* cell ND has simplified lot of conventional XRD experimentation of Li ion cells--ND is one experiment with a real cell as opposed to two separate experiments in XRD with reference electrodes and yet with depth-of-penetration-limitation of XRD. Although the two separate XRD experiments could be combined to provide results similar to ND, there, one can never be certain about one-to-one correlations of phase transitions in anode versus cathode. So this *in situ* electrochemical ND experimentation is a major advancement and realistic with respect to Li-ion cells.

Neutron and X-Ray Scattering Studies of the Liquid-Liquid Transition in Supercooled Confined Water and the Phonon-Like Collective Excitation in Globular Proteins

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Funding: \$350,000 (2014)

PROGRAM SCOPE

Water, the most common liquid on Earth, is indispensable to all the living systems. The mystery of water is buried in its deeply supercooled region where the bulk pure water cannot enter into because of inevitable freezing into ice, referred to as “no man’s land” in the literature. We have extensively studied, using elastic, quasi-elastic (QENS), and inelastic (INS) neutron scattering techniques, the phase behavior and the dynamics of supercooled water by confining water in hydrophilic nanopores of MCM-41-S so that we can supercool water down to this “no man’s land”. We have also discovered phonon-like excitations in a hydrated protein molecule and the dynamic crossover phenomenon in protein hydration water. An important extension of our research during this period is our studies of microstructure of Ordinary Portland Cement (OPC) and the Green Cement (GC). Why “GC”? With a worldwide production of about 3 billion tons/year, cement is the most important building material used in the modern society. Due to the enormous volumes involved, the CO_2 emission in the production process of cement is responsible for about 5% of the total CO_2 emission of human origin -- 40% of which is due to the energy consumption in the process of using it, while the remaining 60% arises from the calcination of limestone

and clays to obtain the mix of calcium silicates and aluminates that constitutes OPC. The cement paste eventually solidifies into a concrete, in it the major binding phase is a gel called calcium silicate hydrate (C-S-H). We have studied this important C-S-H, using neutron scattering technique at various national labs in the US with samples provided by the University of Florence Group. The GC is made of Magnesium Oxide based material and its production process requires lower temperature that results in much less CO₂ emission. In 2014, we have studied multiscale structure of C-S-H gel and magnesium-silicate-hydrate (M-S-H) gel that is the major binding phase of the GC.

FY 2014 HIGHLIGHTS

In the past year, we have made specific significant progress in the study of the deeply supercooled water confined in MCM-41-S through the direct measurement of density of water in the pore using an ingenious SANS method and have published about a dozen referred articles in high-impact journals. We show evidence of the existence of a first-order phase transition from high-density liquid (HDL) to low-density liquid (LDL), and the resultant phase diagram is suggested in several of our publications. In addition, we found that it is possible to explore the existence of the HDL and LDL by another inelastic neutron scattering method and confirmed that the end-point pressure of the Widom line in the one-phase region of the phase diagram is around 1.6 kbar. As to our studies of microstructure of OPC and the GC, with the continuing enthusiastic collaboration with the Florence Group, we have found that the colloidal particles that make up this C-S-H gel to be multilayer disk-like “globules”, whereas for M-S-H gel the globules are polydispersed spherical particles. These prominent differences in basic structure of the two gels can explain why the concrete that are formed from the OPC and the GC have different mechanical strength. This understanding of the microstructure of C-S-H and M-S-H also gives us a clue to possible methods of improving the GC so that its resultant concrete can have a better mechanical strength by certain kinds of additives in the future. This suggests the great potential for further study on this subject in the coming year. During this reporting period, we added two major publications on this topic, and one of my Ph.D. students on this research also graduated in August 2014.

Improper Ferroelectricity and Frustrated Magnetism in Hexagonal Multiferroics: Neutron and Ellipsometry Studies

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Andrei Sirenko; New Jersey Institute of Technology
Students: 3 Postdoctoral Fellow(s), 3 Graduate(s), 0 Undergraduate(s)
Funding: \$270,000 (2014)

PROGRAM SCOPE

Using a complementary combination of neutron scattering and full Muller matrix far IR ellipsometry, we investigate “duality” of improper ferroelectricity and magnetic frustration in hexagonal multiferroics. These systems exhibit an enhanced sensitivity to external fields. We study effects of structural constraints and magnetic geometrical frustration on the ferroelectric, magnetic, and magnetoelectric properties of multiferroics including (RE,In)(Ga,Mn)O₃, REInO₃, and several related systems such as Ca₃CoO₆. Static and dynamic properties of various phases, as well as of structural and magnetic transitions are investigated. The resulting understanding of the microscopic structure, dynamics, and

their relationship to the effects of applied fields should help identify the specific systems with a potential for giant static and dynamic response, and thereby show a prospective approach for discovery of compounds with enhanced properties for future device applications.

FY 2014 HIGHLIGHTS

Multiferroic vortices in the domain patterns of hexagonal manganites have been investigated. Fluctuating vortices were frozen by quenching, imaged, and the obtained patterns analyzed. The obtained results reveal deep theoretical connections between physics of ferroelectrics, superfluids, elementary particles (such as the Higgs boson), and the evolution of the cosmos. In particular, it was found that the dynamics of the phase transitions in the multiferroic manganites follows the predictions of the Kibble–Zurek model for cosmological strings formed in the early Universe. This discovery opens a new avenue for understanding the universal properties of phase transitions in such different subjects are cosmology, high-energy particle physics, and condensed-matter physics. We also studied Mueller matrix spectra of optical phonons in hexagonal multiferroic oxides RMnO_3 , where $R = \text{Ho, Er, Tm, Yb, and Lu}$. Signatures of spin-phonon interaction have been found below the temperature of the antiferromagnetic phase transition T_N due to magnetic ordering of Mn^{3+} spins. A decrease of the ionic radius for R^{3+} ions between Ho^{3+} and Lu^{3+} in the corresponding RMnO_3 compounds resulted in systematic variation of the frequency for several optical phonons.

Using Neutron as a Probe to Study Magnetic Excitations in Strongly Correlated Electron Materials

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Funding: \$720,000 (2014-2016)

PROGRAM SCOPE

Understanding the electronic structure and magnetism in correlated electron materials continues to be at the forefront of modern condensed matter physics. Compounds containing quasilocalized d-electrons and extended f-electrons exhibit a wide range of phenomena, include high transition temperature and unconventional superconductivity. Elucidating the microscopic spin excitations in these systems is central to understand their exotic macroscopic properties, which continue to defy description of the conventional Fermi-liquid theory. Neutron scattering plays an important role in determining the dynamical spin properties in these materials. The normal operation of the spallation neutron source and upgraded high-flux isotope reactor at Oak Ridge National Laboratory has created a unique opportunity for us to establish a strong materials synthesis and neutron scattering program at Rice University. The scope of our present program is to study spin excitations in iron-based superconductors, with the dual purpose of describing magnetic interactions in these materials and, at the same time, training the next generation of neutron scattering scientists. We also establish a materials growth laboratory capable of producing some of the best Fe-based superconductors for the U.S. condensed matter physics community.

FY 2014 HIGHLIGHTS

[1] Discovery of a double resonance in underdoped $\text{NaFe}_{1-x}\text{Co}_x\text{As}$ family of iron pnictides. Phys. Rev. Lett. 111, 207002 (2013). [2] A determination of doping dependence of spin excitations and its correlations with high-temperature superconductivity in iron pnictides. Nature Communications 4, 2874 (2013). [3] A determination of the effect of Pnictogen Height on Spin Waves in Iron Pnictides. Phys. Rev. Lett. 112, 217202 (2014). [4] Magnetic anisotropy in underdoped NaFeAs family of superconductors. Phys. Rev. B 90, 140502(R) (2014).

Vortex Lattices Studies in Type II Superconductors

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Sr. Investigator(s):
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Funding: \$150,000 (2014)

PROGRAM SCOPE

The program centers on the study of vortices and the vortex lattice (VL) in type-II superconductors and has two main themes. The first is fundamental studies of superconductivity. The formation and condensation of Cooper pairs varies for different materials, and in many cases the exact microscopic mechanism remains elusive. An important step towards a microscopic understanding is detailed knowledge of the order parameter. This is especially important in materials such as UPt_3 and Sr_2RuO_4 where the carriers in the Cooper pairs are believed to form a triplet, but where the detailed order parameter is not well established. We use the vortices to probe the intrinsic nature of the superconducting state in unconventional and/or new materials. The second theme is the study of vortex matter dynamics and in particular the recently discovered metastable VL phases in MgB_2 . Vortex motion will lead to dissipation and is responsible for limitations in the critical electrical current density and of direct importance to the practical use of superconductors. However, the VL metastability is not due to traditional vortex pinning and instead it appears to be due to VL domain effects. This has opened up a new direction in the study of vortex dynamics with analogues to jamming in granular materials.

FY 2014 HIGHLIGHTS

We have used small-angle neutron scattering (SANS) to study the VL in a number of superconductors within the scope of the project. Our earlier measurements of the intrinsic superconducting anisotropy in Sr_2RuO_4 found this to be much larger than the upper critical field anisotropy. This suggests either a subtle coupling between the magnetic field and the triplet order parameter proposed for this material, or Pauli limiting, which is inconsistent with triplet pairing with the Cooper pair zero spin projection along the c -axis. Extending these measurements we found the superconducting anisotropy to be independent of applied field and temperature, lending further support to a Pauli limiting scenario and imposing significant constraints on possible models of (triplet) pairing. In UPt_3 the superconducting phase diagram has three distinct mixed (vortex) phases that can only be explained by unconventional superconductivity. Multiple models for the order parameters in this material have been proposed, all with nodes in the superconducting energy gap and different nodal structure in the three vortex phases. We have measured the temperature dependence of the components of the London penetration depth

that probe the gap nodal structure along the principal directions of the crystal finding a linear behavior in the low temperature limit. Our measurements are consistent with calculations based on an order parameter with E_{2u} symmetry. To investigate the mechanism responsible for the metastability in MgB_2 we have studied the dynamics with which the VL is driven to the ground state by successive applications of small-amplitude AC magnetic field oscillations. We observe a crossover from a slow to a fast power law indicates a two-step process, possibly beginning with a nucleation of ground state VL domains followed by their rapid growth once the VL domain walls reach a critical density. This supports the hypothesis that the metastability may be due to a VL domain jamming.

Vibrational Thermodynamics of Materials at High Temperatures

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Students: 1 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding: \$190,001 (2014)

PROGRAM SCOPE

This is a study of entropy, the central issue in thermodynamics. Most of the entropy of materials comes from atom vibrations, and this is a project to understand the origin of vibrational entropy. With accurate assessments of entropy, we assess its effects on the thermodynamic stability of phases in materials and on phase transformations. The work is designed to address cases where vibrational entropy is expected to be large and interesting, especially at high temperatures where there can be significant effects from anharmonicity and electron-phonon interactions. It is primarily an experimental investigation of materials at high temperatures, using inelastic neutron scattering performed at national user facilities such as the Spallation Neutron Source, ORNL. Inelastic neutron scattering, with support from computation, is the most powerful approach today for quantifying the different contributions to vibrational entropy. The experimental measurements give vibrational spectra of the materials, i.e., their phonon densities of states (DOS). With accurate phonon DOS curves, we can obtain the vibrational entropies of different materials, or measure changes in vibrational entropy with temperature or chemical composition. From neutron scattering measurements on single crystals we can obtain a more detailed picture of why phonons undergo changes with temperature. The underlying reasons for differences in DOS curves and entropies are obtained from computational methods such as *ab initio* molecular dynamics simulations, but we still use perturbation theory for useful insights. At high temperatures there is a hierarchy of anharmonic effects, and we have methods for separating them into quasiharmonic entropy, anharmonic entropy, and effects of electron-phonon interactions. Negative thermal expansion associated with highly anharmonic behavior is also of interest in some of the proposed investigations.

FY 2014 HIGHLIGHTS

Ph.D. Thesis completed: Tian Lan, Ph.D. in Applied Physics, May 6, 2014. Hillary L. Smith, Ph.D. in Materials Science, May 29, 2014. Publications: [1] Thermodynamic modelling of crystalline unary phases M. Palumbo, B. Burton, A. Costa e Silva, B. Fultz, B. Grabowski, G. Grimvall, B. Hallstedt, O. Hellmann, B. Lindahl, A. Schneider, P.E.A. Turchi, and W. Xiong, *Physica Status Solidi B* 251, 1432 (2014). Lattice vibrations usually give the major contribution to $G(T)$. They are treated in detail for aluminum with

neutron scattering studies and first principles calculations. Results were in excellent agreement with those of conventional calorimetry. [2] Anharmonic lattice dynamics of cuprite Ag_2O studied by inelastic neutron scattering and first principles molecular dynamics simulations T. Lan, C.W. Li, J.L. Niedziela, H. Smith, D.L. Abernathy, G.R. Rossman, and B. Fultz, Phys. Rev. B 89, 054306 (2014). Inelastic neutron scattering measurements on silver oxide (Ag_2O) with the cuprite structure were performed at temperatures from 40 to 400 K. The calculated negative thermal expansion and the lattice dynamics were in excellent agreement with the neutron scattering data. We report rich anharmonic interactions between Ag-dominated phonon modes and O-dominated modes. [3] Phonon anharmonicity of monoclinic zirconia and yttrium-stabilized zirconia at elevated temperatures Chen W. Li, H. Smith, T. Lan, J.A. Munoz, J.B. Keith, L. Mauger, D. Abernathy, and B. Fultz, Phys. Rev. B, submitted. Inelastic neutron scattering measurements of monoclinic zirconia (ZrO_2) and 8 mol% yttrium-stabilized zirconia were performed at temperatures from 300 to 1373 K. Large anharmonicity was found, especially for phonon modes dominated by the motions of oxygen atoms. [4] Phonon Anharmonicity in Silicon from 100 to 1500 K D.S. Kim, H.L. Smith, J.L. Niedziela, C.W. Li, D.L. Abernathy, and B. Fultz, Phys. Rev. B, submitted. Inelastic neutron scattering was performed on silicon powder.

Neutron Scattering Studies of Classical and Quantum Fluids in Nanoporous Media

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Students: 0 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding: \$150,000 (2014)

PROGRAM SCOPE

We conduct unique, world class neutron scattering measurements of Bose-Einstein condensation (BEC), atomic momentum distributions and the collective modes of quantum liquids. This is both in bulk liquid ^4He and in liquid ^4He confined in nanoporous media where superfluidity, BEC and the collective phonon-roton (P-R) modes are substantially modified. Also, liquid ^4He in porous media is an example of nanoscale Bosons in disorder. BEC, superfluidity and sharply defined modes are the three most fascinating properties of liquid ^4He . Interest in BEC and superflow also reaches across condensed matter (e.g. superconductivity, BEC in quantum gases and reduced dimension systems). BEC and P-R modes are uniquely measured using neutrons. We bring unique neutron scattering data on BEC and modes for comparison with superfluidity measurements to reveal the interdependence of BEC and superfluidity. As a recent achievement, we note that there are two renowned theories of superfluidity, quite different and each with specific domains of application. In the first, the Landau theory, superflow follows from the existence of a well-defined P-R mode supported by dense liquid ^4He . In the second, superflow is a manifestation of BEC and phase coherence in the liquid. We present combined measurements of superfluidity, BEC and phonon-roton modes in liquid ^4He confined in the porous medium MCM-41. The results integrate the two theories by showing that well-defined P-R modes exist where there is BEC. In porous media, the critical temperature for superfluidity, T_c , is suppressed below that for BEC. The measurements show that BEC and well-defined P-R modes co-exist. The two are common properties of a Bose condensed liquid and either can be used as a basis of a theory of superfluidity. In addition, the disorder in the porous medium creates a localized BEC 'phase' consisting of islands of BEC and P-R modes.

FY 2014 HIGHLIGHTS

The goal of this program is to reveal the interdependence of Bose-Einstein condensation (BEC), well-defined, collective phonon-roton (P-R) modes and superfluidity in liquid ^4He confined in porous media. It is particularly to determine how BEC and P-R modes create superfluidity. BEC and modes are uniquely observable using neutrons. We have recently made the first ever successful measurements of the Bose-Einstein condensate fraction of liquid ^4He in any porous media at the Spallation Neutron Source (SNS) in collaboration with S. O. Diallo (SNS), R. T. Azuah (NIST Center for Neutron Research) and D. L. Abernathy (SNS). These measurements of BEC show unequivocally that well-defined P-R modes exist where there is BEC (in the same temperature range). This confirms the theory which proposes that well-defined P-R modes exist because there is BEC. We have also measured the P-R modes in porous media, chiefly at the Institut Laue Langevin, in collaboration with J. Bossy, J. Ollivier and H. Schober and made path integral Monte Carlo (PIMC) calculations of the BEC condensate fraction and the superfluid fraction of liquid ^4He in pores to interpret these measurements. There are two competing theories of superfluidity: one based on the existence of well-defined P-R modes proposed by Landau (1941 and 1947) and the other based on BEC and consequent phase coherence in the fluid proposed initially by London (1938). The present measurements show that BEC and P-R are common properties of a Bose condensed fluid so that the two theories are really complementary rather than competing pictures of superfluidity. Fourthly, on a quite different topic, we have shown how the intrinsic motional dynamics in proteins can be obtained from neutron scattering experiments, dynamics that are independent of the instrument energy resolution and the scattering wave vector used.

Crystal Growth and Scattering Studies of Model Cuprate Superconductors

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Students: 1 Postdoctoral Fellow(s), 1 Graduate(s), 2 Undergraduate(s)
Funding: \$750,000 (2014-2016)

PROGRAM SCOPE

The goal of this effort is the crystal growth and comprehensive investigation of the $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$ cuprates, arguably the most desirable unconventional superconductors due to their record transition temperatures (T_c) and their relatively simple crystal structures. The hope is to conclusively identify the minimal model required for a proper theoretical description of the enigmatic cuprates. Our group remains the only one in the world to have mastered the growth of sizable single crystals of $\text{HgBa}_2\text{CuO}_{4+\delta}$ (Hg1201), the simplest ($n=1$) member of this materials family. The proposed work will build on our demonstration, using neutron scattering, of unusual translational-symmetry-preserving ($q=0$) magnetism in the pseudogap phase of Hg1201. These magnetic neutron scattering results will be extended over a wide range in parameter space (energy, momentum, temperature, hole concentration) and, in particular, include the antiferromagnetic response. They will furthermore be complemented by transport and synchrotron X-ray measurements of the charge degrees of freedom. In addition, the growth and study of the $n=2$ member of the Hg-family of cuprates will be explored. Last, but not least, the work will continue to aim to have a far-reaching impact beyond the neutron, X-ray and transport experiments led by the PI through collaborations with experts using complementary experimental tools.

FY 2014 HIGHLIGHTS

A seemingly universal feature of the antiferromagnetic (AF) excitation spectrum of the cuprates is the hourglass dispersion. Using neutron scattering, we discovered that this feature is absent in Hg1201 ($T_c=71\text{K}$), and that the AF fluctuations in Hg1201 can be rather impervious to the onset of superconductivity, with a spectrum that is dominated by a large susceptibility peak at about 50 meV that onsets at the much higher pseudogap temperature ($T^*\approx 300\text{K}$). Furthermore, the onset of substantial AF fluctuations correlates with the appearance of quasistatic $q=0$ order below T^* . These findings constitute a dramatic departure from the notion that an hourglass-shaped spectrum associated with charge-spin stripe fluctuations is a universal feature of the cuprates [preprint]. For nearly three decades, it has often been argued that the cuprates are unconventional metals. One influential experimental result had been the apparent violation of Kohler's rule for the magnetoresistance. In stark contrast, we discovered that the simple tetragonal model compound Hg1201 beautifully obeys Kohler's rule in the pseudogap regime, with a Fermi-liquid scattering rate. We were furthermore able to show that Kohler's rule is in fact hidden in other cuprates [Phys. Rev. Lett. (2014); editor's suggestion]. Our planar resistivity measurements of underdoped Hg1201 in high magnetic fields demonstrated the universality of quantum oscillations, and thus allowed us to rule out that quantum oscillations in Y-based cuprates are a materials-specific property [Nature Physics (2013)]. Using resonant X-ray scattering, we observed subtle short-range charge-density-wave order in the same samples that exhibit quantum oscillations, which allowed us to demonstrate a simple universal connection between the ordering wave vector and Fermi-surface area associated with the oscillations [Nature Commun. (2014)]. Our initial efforts to synthesize Hg1212 ($n=2$) have yielded small crystals.

EARLY CAREER: Neutron Scattering Instrumentation Research and Development for High Spatial and Temporal Resolution Imaging at Oak Ridge National Laboratory

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Students: 2 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding: \$150,000 (2014)

PROGRAM SCOPE

Neutron scattering facilities like those available at Oak Ridge National Laboratory are enabling the discovery and development of advanced materials including those to be used for next generation energy storage systems. In spite of all the success that neutron imaging has enjoyed in recent years, even higher-impact research is limited by the current temporal and spatial resolution of neutron detection devices. In particular, the spatial resolution of all neutron imaging methods in use and under development is fundamentally limited by the variance introduced by the charged particles emitted from neutron absorption. Thus, we are investigating, designing and demonstrating an array of $\sim 1\ \mu\text{m}$ -sized glass scintillating fibers arranged via photonic-crystal-fiber patterning techniques— with particle tracking (a must) so that position resolution can be finer than that allowed by the charged particle ranges. The processes, knowledge and algorithms developed will allow for spatially ($1\ \mu\text{m}$) and time resolved ($<100\ \text{ns}$), high throughput neutron transmission imaging in large areas at reasonable costs in the near term.

FY 2014 HIGHLIGHTS

Two microstructured glass scintillator arrays were fabricated, and testing began on a neutron beamline at HFIR. Scintillation of micron-sized scintillator was observed. These arrays were modeled using Monte Carlo methods, and the ideal performance was predicted. Reconstruction algorithm development has begun based upon the results of Monte Carlo simulations.

Neutron Scattering Studies of Cobaltite Crystals and Heterostructures

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Funding: \$150,221 (2014)

PROGRAM SCOPE

Complex oxide materials such as perovskite cobaltites provide enormous challenges to our fundamental understanding of electrons in solids, in addition to outstanding potential for applications in a range of technologies. This project is aimed at two of the biggest challenges that have emerged in this area - the need for a fundamental understanding of the electronic and magnetic behavior in complex oxides, and a full appreciation of what we can achieve via an understanding of the physics, materials science, and chemistry, of complex oxide interfaces and heterostructures. We are tackling these questions using a single family of materials (the doped cobaltites) as an illustrative example, trying to understand nanoscopic magneto-electronic phase separation, spin-state transitions, insulator-metal transitions, and the influence of interfaces, defects, and strain on magnetism and transport. The research is thus very broadly relevant, touching upon catalysis, solid oxide fuel cells, data storage devices, oxide spintronics, and the general development of oxide electronics. We are carrying out a collaborative and interdisciplinary approach to understanding magnetism and transport in these materials, bringing to bear a battery of complementary measurement techniques, exploiting the full power of neutron scattering, and capitalizing on expertise in synthesis and characterization of both bulk and thin film oxides.

FY 2014 HIGHLIGHTS

In 2014, progress was made in four main areas: Understanding nanoscale inhomogeneity in lightly doped cobaltites, the physics of narrow electronic bandwidth cobaltites, cobaltite films and heterostructures, and magnetic inhomogeneity in complex alloys. In the first, we focused on lightly doped (La,Sr)CoO₃ to understand how magnetic polarons forming at light doping evolve into ferromagnetic clusters at higher doping. We have developed an understanding of this crossover, emphasizing its statistical nature, and the key role of spin and charge dynamics. In the second area, narrow bandwidth cobaltites, systems such as Pr_{1-x}Ca_xCoO₃ have been studied, in order to understand (a) the interplay between phase separation and spin-state, and (b) the Pr-based compounds recently discovered to undergo first-order transitions where the Pr valence abruptly shifts. In the third area, cobaltite films and heterostructures, a number of findings have come to light, including a full appreciation of how oxygen vacancy ordering serves as a mechanism of lattice mismatch accommodation. This creates a link between strain and stoichiometry, which we exploited to demonstrate strain and orientation manipulation of this defect ordering, and the associated oxygen

depth profile. Most importantly, subsequent tuning of the interfacial magnetic and charge transport properties has been demonstrated. In addition to establishing a new means to tailor interfacial properties of complex oxides, the results point to new phenomena emerging under oxygen vacancy ordering. Finally, the approach used to study nanoscale magnetic inhomogeneity has been extended to other systems exhibiting these effects, including complex metal alloys such as off-stoichiometric Heuslers. Neutron scattering provided detailed insight into the magnetic behavior of these materials, establishing a number of important points of connection with strongly correlated oxides.

Local Complexity and the Mechanics of Phase Transitions in Novel Materials

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Funding: \$760,000 (2014-2016)

PROGRAM SCOPE

The scope of this program is to investigate novel materials that provide unique opportunities to study emergent exotic states of matter that arise from the intricate coupling of the electronic and lattice degrees of freedom, and of their implications in the mechanics of phase transitions. Central to this project is the exploration of distinct features such as the coexistence of two (or more) order parameters, the nucleation of different phases in the parent matrix, spin/charge density waves, and the formation of structural patterns that break the global symmetry and present even at equilibrium conditions. These are key components to our understanding of the evolution across phase boundaries. However, they cannot be readily characterized with traditional means used for probing single electron behavior. This is because their behavior is a collective effect, in response to strong interactions. The goal of the proposed program is to explore such states of matter that appear to be endemic in oxides, superconductors and intermetallic compounds using scattering techniques.

FY 2014 HIGHLIGHTS

In the 2014 fiscal year, our studies on Mott systems such as LaNiO_3 provided evidence for a continuous cross-over across the quantum critical point in nickelates. Monoclinic droplets dispersed randomly in the lattice tend to be insulating and can explain the presence of a pseudo gap in this metallic system. We have also completed a very detailed study of orbital ordering in magnetic vanadates and evidence has been provided to support the presence of G-type orbital ordering above the transition. With doping the ordering changes to C-type. In the insulating antiferromagnet of SrFeO_2 , we observed the magnetic exchange coupling to be very sensitive to a local mode involving transverse displacements of O and Fe. On the Fe superconductors, we have been investigating the issue of phase separation in $\text{K}_x\text{Fe}_{2-\gamma}\text{Se}_2$. This work is still ongoing with many new single crystals grown and measured using neutrons for further analysis. We have also been making Ba and Ca doped FeSe using the new ammonia synthesis. Frustrated systems such as $\text{Ba}_3\text{CuSb}_2\text{O}_9$ and LuMnO_3 have provided us with a venue to explore the intricate interplay of spin and lattice interactions.

Understanding Functional Lyotropic Liquid Crystal Network Phase Self-Assembly and the Properties of Nanoconfined Water

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Funding: \$160,000 (2014)

PROGRAM SCOPE

Lyotropic liquid crystals (LLCs), a class of nanostructured soft materials comprising structurally periodic aqueous and hydrophobic nanodomains lined with well-defined chemical functionalities, stem from the self-assembly of small molecule amphiphiles in concentrated aqueous media. Potential applications of LLCs include advanced separations membranes, templates for mesoporous inorganic oxide catalysts, and ion transporting membranes for fuel cells and batteries. Network phase LLCs with percolating 3D-networks of monodisperse, water-filled nanopores (~0.5-2 nm in diameter) are particularly desirable in many of these applications. Through a synergistic combination of new amphiphile syntheses, characterization of their aqueous LLC phase behavior using small-angle scattering techniques, and molecular dynamics (MD) simulations of these self-assembled structures, Mahanthappa and Yethiraj are developing guiding principles for rational design of surfactants that preferentially form LLC network phases. Our studies focus on identifying specific molecular attributes of bis(sulfonate) and bis(phosphonate) gemini ("twin tail") surfactants that drive their preferential self-assembly into LLC networks. Since MD simulations suggest that surfactant headgroup-counterion correlations crucially govern LLC phase selection, we are using neutron and X-ray scattering methods to assess the validity and generality of this self-assembly model. We are also using wide-angle and quasielastic neutron scattering to investigate how pore functionality, geometry, and diameter affect the structure and dynamics of water nanoconfined within LLCs. By correlating nanoconfined water properties with the ionic conductivities of bis(sulfonate) and bis(phosphonate) LLCs, we aim to identify new molecular design criteria for next-generation ion transporting membranes for solar fuels generation and utilization.

FY 2014 HIGHLIGHTS

By synthesizing several new bis(sulfonate) gemini surfactants and rigorously characterizing their aqueous LLC phase behaviors, we have demonstrated that the gemini architecture enables the formation of network phase LLCs unavailable from conventional, single-tail sulfonate amphiphiles. Electrochemical impedance spectroscopy measurements demonstrate that gemini bis(sulfonic acid) LLCs, in which sulfonic acid moieties decorate water-filled nanopores with diameters ~1-2 nm, exhibit exceptionally high proton conductivities. Against conventional wisdom, our initial studies suggest that pore wall acidity and proton conductivity are not necessarily correlated. Instead, we hypothesize that pore functionality affects nanoconfined water structure and dynamics in a manner that significantly contributes to the observed high proton conductivities. Comparative molecular dynamics simulations have established that the parity of the length of the hydrophobic linker in gemini dicarboxylate surfactants controls the allowed conformations of the hydrated surfactant, whereby odd carbon linkers disallow the formation of both lamellar and hexagonal LLC phases in favor of the double gyroid network phase. However, preliminary simulations indicate that the effects of linker length parity are much less

significant in bis(sulfonate) surfactants. Ongoing simulations aim to understand the origins of these differences in the LLC self-assembly behaviors of dicarboxylate and bis(sulfonate) surfactants.

Engineering and Doping Profiles in Organic Semiconductor Materials

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PROGRAM SCOPE

We establish p-type doping gradients in conjugated polymers with potential applications towards organic electronic devices. The goal of the proposal is to develop methods to produce thermally persistent non-uniform doping profiles in organic materials. Doped organic semiconductors are currently unsuitable for device applications because organic dopants diffuse and drift at low temperatures, destroying device function. We address this problem by synthesizing chemically tailorable dopants that are designed for processability. The specific aims of this proposal are: (a) to determine the p-type doping effectiveness of neutral dopants in conjugated polymers, (b) to synthesize a family of p-type dopants for organic films with side groups that can be optimized for solubility and doping effectiveness (c) to use the functionalized dopants to generate non-uniform doping profiles and study the thermal persistence of the dopant, and diffusion mechanism. (d) to develop neutron and x-ray methods to measure the dopant distribution profile, dopant diffusion rate, and doping effectiveness. To achieve these aims, we synthesized a family of p-type dopants based on the F4TCNQ molecule. Specifically we exchanged the cyano group on the F4TCNQ for an ester that can be functionalized with side chains to affect solubility. We then used these dopant molecules to fabricate doping gradients with high precision. We found that dopants cause strong reduction in the solubility of the polymer in common non-polar solvents. We used dopant induced solubility control (DISC) to develop a scalable conjugated polymer patterning process that can be optically controlled. We have also used neutron scattering techniques (BASIS, GP-SANS, VISION) to study the interaction of the polymer P3HT with the dopant F4TCNQ. X-ray spectroscopy is being used to determine the electronic structure of the dopant and polymer in order to constrain the structural model needed to fit the VISION data.

FY 2014 HIGHLIGHTS

The Moule group published one article in 2014 titled "Material Profile influences in bulk-heterojunctions" in Journal of Polymer Science B. The article quantifies vertical concentration in organic PV layers comparing results from electron tomography, x-ray reflectometry, and neutron reflectometry. We filed for a provisional U.S. patent for the invention of a conjugated polymer patterning method. Our first article on this method was accepted in ACS-nano in December 2014. We developed separate Materials Transfer Agreements with LBNL Molecular Foundry and Cambridge Display Technology Inc. for high quality conjugated polymers related to the patterning technique. We received measurement time for the BASIS, VISION, and GP-SANS beam lines at SNS. On VISION we acquired enough data for 1-2 publications comparing the vibrational states of doped and undoped polymers. We are now working on modeling of the data in collaboration with Thomas Proffen from CNMS. Our BASIS time was delayed due to beam outage. The GP-SANS sample holder failed in the first measurement and samples will be re-

measured in January with improved solvent seals. We received measurement time at ALS to perform NEXAFS on doped polymer samples. The element specific data is ideal to constrain molecular models of doped states. We studied the vertical diffusion of dopant/polymer and dopant small/molecule systems as a function of temperature, dopant strength, and dopant size. Results of this study are being prepared for publication. We synthesized a series of dopants with side chains designed to alter the diffusion rate and miscibility of the dopants. We found that dopants with side chains are significantly more miscible but have reduced diffusion rate due to increased size. Also di-substituted dopants do not have a -1 state but rather only a 2- state due to symmetry changes to the TCNQ with the addition of two esters. A first publication on new dopants is in preparation.

Thermodynamics of Self-Assembly in Globular Protein-Polymer Conjugates

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Funding: \$720,000 (2014-2016)

PROGRAM SCOPE

Engineering enzymes and optically active proteins into bioelectronic devices for the production of H₂, the reduction of CO₂, or the production of biofuels allows the evolutionarily optimized performance of the protein to be exploited to produce high-performance biomolecular variants of catalysts. Engineering biocatalytic materials requires achieving a high protein activity and active site density, controlling substrate/product transport through the material, maintaining protein stability, and developing low-cost processes for material fabrication. Analogous to synthetic catalysts or organic electronics, this requires the arrangement and orientation of the protein at an interface between two phases that provide for the transport of each reagent or charge carrier. The self-assembly of block copolymers containing an enzyme or optically active protein block provides a bottom-up method to produce nanostructures that simultaneously achieve control over transport through two phases and yield a high density of oriented protein at an interface. This project investigates the fundamental structure and thermodynamics of block copolymer systems containing a globular protein block, enabling the production of functional nanomaterials. Both the folded protein chain shape and the specific interactions between globular proteins differ significantly from the Gaussian coil block copolymers, adding significant complexity to the phase behavior of these systems. Despite this complexity, we hypothesize that universal rules of self-assembly may be elucidated for these protein-polymer hybrids, and in the past two years we have addressed three fundamental questions: (1) How is the phase behavior for a protein-polymer conjugate different than that of traditional block copolymers? (2) What is the effect of protein shape (steric interactions) on self-assembly? (3) What is the effect of protein-polymer interactions on self-assembly?

FY 2014 HIGHLIGHTS

To explore the effect of protein interactions on self-assembly, a carefully controlled experiment was performed to compare the self-assembly of mCherry and EGFP conjugates. The red and green fluorescent proteins have little primary sequence homology and consequently significantly different electrostatic and hydrophobic surface potential distributions; however, they have similar sizes, shapes, and second virial coefficients. When conjugates with the same molar mass Poly(N-isopropylacrylamide)

(PNIPAM) were prepared for both proteins, self-assembly was largely identical. A further experiment was performed to mutate mCherry, systematically altering its electrostatic surface potential. Again, only minimal effects on the order-disorder transition concentration, symmetry of nanodomain structure, and domain spacing were observed. Comparison of self-assembly for conjugates with different polymer types illustrates that protein-polymer interactions are critical to the self-assembly of these systems. Comparing PNIPAM conjugates to those with poly(hydroxypropylacrylate) (PHPA) and poly(oligoethyleneglycolacrylate) (POEGA) illustrates the ability to form previously unobserved phases, including a cubic phase consistent with a gyroid structure, and the ability to tune the Order-Disorder Transition (ODT) based on protein-polymer interactions. To follow up on this observation, two separate methods are currently under development for quantifying these protein-polymer interactions: form factor analysis of conjugates in dilute solution and partial structure factor decomposition analysis of protein-polymer blends with varied H₂O/D₂O solvent systems, enabling quantitative extraction of the protein-polymer structure factor which can then be modeled as a function of interactions.

From Interfaces to Bulk: Experimental-Computational Studies Across Time and Length Scales of Multi Functional Ionic Polymers

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Funding: \$182,421 (2014)

PROGRAM SCOPE

Neutron scattering coupled with computational studies have been carried out to resolve the structure and dynamics at the interfacial regions of ionic structured co-polymers. Structured ionic polymers with their large size and complexity offer superb media to tailor multiple desired properties into one molecule to form multifunctional materials. The interfacial regions between segments with different chemical nature, such as hydrophilic and hydrophobic, within structured polymeric complexes often control their properties and their responses to changes in the environment. These potentially responsive multifunctional materials is a key to the development of next generation of smart materials for clean energy generation and storage, self-healing layers and drug delivery media; all in the core of the national needs. A conjunction of experimental and computational studies has been carried out on a series of polymers whose chemical architecture is systematically tailored to target controlled changes at the interfaces. Specifically we investigate a pentablock that consists of t-methyl styrene, bound to randomly sulfonated polystyrene by polyethylene propylene. Dvora Perahia from Clemson has been leading the experimental effort and Gary S. Grest from Sandia co-directs the computational studies. Structural features ranging from 0.1nm to 100 nm have been identified by neutron and x-ray scattering/reflectivity. Dynamics across the time window that incorporates the motion of the polymer, ions and solvents across a length scale of 0.1 to ~30 nm is captured by quasielastic neutron studies including spin echo and quasielastic neutron backscattering probing the time range from ~0.1 to 100 nsec. Molecular dynamic simulations of model polymers identical to those studied experimentally provide molecular understanding of the structure and dynamics and explore length and time scales that can not be probed by the experimental tools.

FY 2014 HIGHLIGHTS

Work had been carried out along several pathways including solutions and thin film using scattering, atomistic and coarse grained computational studies, as well as computational methodology developments. Experimental Neutron studies SANS of dilute solutions of cyclohexane/heptane were completed and are in review at the Journal of Soft Materials. This study defined the structure of the pentablock in dilute solution from that of an individual molecule to that of a micelle. One of the major goals of the work is to resolve the dynamic processes that underlie the transport within complex polymers containing ionic groups. With the ultimate goal of resolving the dynamics of complex ionomers we construct three separate interfaces including poly-styrene-polystyrene sulfonated (Etampawalla *et al*, submitted to J. Chem. Phys.); polystyrene/polyethylene and polyethylene polystyrene sulfonate which will be compared with the pentablock's behavior. The degree of interpenetration as a function of time is resolved for polystyrene/polystyrene sulfonate where only limited interdiffusion is observed. Computational The structure of a single molecule in solvents, parallel to the neutron scattering study was resolved (Aryal *et al*. Communication in Macromolecular Theory and Simulation 2014). We have shown that the overall conformation is solvent depended and where the ionic block remains collapsed under experimental conditions. In Parallel, we have developed a course graining methodology for polystyrene, that is essentially transferable to t-butyle polystyrene, (Macromolecules, Agrawal *et. al*. 2014). In addition we were able to resolve for the first time the structure of the ionic clusters in polystyrene sulfonate (Agrawal *et. al*. In review in PRL). The results were also presented at the American Physics Society meeting 2014, including an Invited (Dvora Perahia) presentation that demonstrated the understanding that coupling between neutron studies and commutations can achieve.

EARLY CAREER: Neutron Scattering Investigation of the Relationship between Molecular Structure, Morphology and Dynamics in Conjugated Polymers

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Funding: \$175,000 (2014)

PROGRAM SCOPE

Conjugated polymers (CP) are enabling technologies including organic photovoltaic cells (OPVs), batteries, thermoelectric energy devices and flexible displays (OLEDs). Unique properties of CPs include simplified processing, synthesis from abundant raw materials, flexibility and a capacity to fine-tune energy levels. Unfortunately, CPs are insoluble and difficult to process. It is common practice to add substitution moieties (e.g. linear, branched and cyclic hydrocarbon groups) to the CP backbone in order to boost solubility without affecting the optoelectronic properties. Yet, little fundamental knowledge has been gained on how these side-groups interfere with self-assembly and/or with charge propagation in nanostructured CP phases and in the solid-state. Currently, there are no mechanisms available to design CP structures from fundamental principles for use in specific applications. We are using a comprehensive suite of neutron scattering techniques coupled with simultaneous (in-situ) property evaluation to develop accurate structure-property relationships to enable effective molecular design. Our four project objectives are: 1) to evaluate the influence of chain architecture on solution conformation, 2) to determine the influence of molecular structure on CP self-assembly, 3) to measure

and correlate dynamic motions of CPs in self-assembled structures (i.e. organogels) and 4) to correlate dynamic molecular relaxations and macroscopic properties of CPs in the solid state. The project is also complemented by advanced molecular simulations to fully understand relationships between chain structure, mesoscale morphology, dynamic relaxations and macroscopic properties. Through the completion of this fundamental investigation we are informing scientists and engineers actively working on the synthesis of novel polymer architectures so that they can achieve simple processing and optimized properties via rational molecular design.

FY 2014 HIGHLIGHTS

Initial quasi-elastic neutron scattering experiments and molecular dynamics simulations were completed to determine the effect of alkyl chain length for poly-alkyl-thiophene derivatives on the solid-state dynamics and electronic properties. New types of high surface area organic-dispersible PEDOT and polypyrrole materials were also developed and their use in cathodes for Li ion batteries has been evaluated. These experiments are ongoing and publication is expected in 2015. Below are the highlights corresponding to 2014 publications. [1] Accurate control over P3AT organogel structure and properties was demonstrated via use of solvent quality to modify self-assembly. It was demonstrated that a clear optimum value in conductivity was achieved, for each material, at specific and unique self-assembly conditions. Newbloom GM, de la Iglesia P, Pozzo LD. *Soft Matter*, 2014, Nov 28; 10 (44), 8945. [2] The internal structure of P3HT/fullerene nanoparticle dispersions was modified by control of composition and synthesis conditions. These dispersions are ink precursors for 'painted' solar cells. Small angle neutron scattering is used to probe internal structure while conductive AFM is used to evaluate photoconductive properties. Richards JR, Whittle CL, Shao G, Pozzo LD. *ACS Nano*, 2014, 8 (5), 4313. [3] The conformation of dilute solutions of poly-3-alkyl-thiophenes is probed with neutron scattering and optical spectroscopy in several solvents and with different alkyl substitution moieties. It is determined that color changes that occur upon dissolution in solvents are controlled by the polarity and structure of solvent molecules and not by conformational changes, which was the more accepted hypothesis. Molecular dynamic simulations are used to validate the neutron scattering results and to probe differences in solvation shells around the polymers. Newbloom GM, Hoffmann SM, West AF, Gile MC, Sista P, Cheung HC, Luscombe CK, Pfaendtner J, Pozzo LD. *Langmuir* DOI: 10.1021/la503666x.

Inelastic Neutron and X-Ray Scattering Investigations of Electron-Phonon Effects in Quantum Materials

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PROGRAM SCOPE

Many quantum materials, i.e. materials where quantum effects are crucial for key properties, often undergo phase transitions driven by electronic charge and/or spin fluctuations. These fluctuations influence electrical and thermal conductivity, specific heat, thermal expansion, etc. Coulomb/magnetoelastic coupling of charge/spin fluctuations to the atomic lattice can induce competing or mutually reinforcing phenomena such as real or incipient structural phase transitions and superconductivity. My group focuses on inelastic scattering of neutrons (INS) or x-rays (IXS) from atomic

lattice fluctuations coupled to charge/spin fluctuations associated with real and/or incipient phase transitions in quantum materials. These lattice fluctuations are either phonons or incoherent fluctuations. The long-term goal of our research is to learn how use observed features of lattice dynamics spectra as markers of microscopic physics of quantum materials responsible for their macroscopic properties of fundamentals and practical interest. The work proposed for the next 3 years has the following themes that feed off each other: 1. Extending Multizone phonon refinement pioneered by us to a bigger class of materials. 2. Experiments to systematically measure electron-phonon effects in order to understand and eventually control charge order and fluctuations, structural phase transitions, and polarons. 3. General insights into electron-electron and electron-lattice interactions. Item 1 fits into the BES mission to operate major scientific user facilities because it serves to amplify the capabilities of the SNS and items 2,3 fit into the DOE Basic Energy Sciences (BES) program's mission to understand, predict, and ultimately control matter and energy at the electronic, atomic, and molecular levels.

FY 2014 HIGHLIGHTS

During the previous period we 1) directly measured the spectrum of dynamic charge stripes for the first time; 2) found evidence of a novel charge collective mode that correlates with the superconducting T_c in a family of copper oxides; 3) clarified the origin of the kink in electronic dispersions in cuprates, 4) Identified a previously unknown spurious feature that can contaminate neutron scattering spectra near 17meV energy transfer. 5) Developed a new Multizone Phonon Refinement (MPR) time-of-flight data analysis technique that clearly resolves phonon branches separated by as little as 10% of the energy resolution by using data from all measured Brillouin zones. Thanks to MPR an efficient and systematic search for electron-phonon effects in a wide variety of materials is now possible. This work resulted in 6 peer-reviewed publications.

Neutron and X-Ray Studies of Spin and Charge Manipulation in Magnetic Nanostructures

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Funding: \$360,000 (2014)

PROGRAM SCOPE

Electronic and magnetic materials are some of the most important and highly tunable materials systems with a wide range of new scientific discoveries. Understanding of the dynamics and the fundamental nanoscale physics of these materials is a crucial cornerstone for developing ways in which electronic and magnetic order parameters can be designed, controlled and manipulated. By combining skills in neutron and synchrotron techniques with sample fabrication, magnetic and transport measurements in films, nanostructures and devices we probe fundamental properties of nanoscale magnetic materials. The proposed and ongoing research has two research thrusts: (1) Time-dependent studies of magnetic nanostructures This research probes the physics of magnetic nanostructures by studying the underlying excitations of the system with atomic depth resolution and nm lateral resolution. The time scales, physics to be studied and techniques used are divided into three distinct regimes: (i) Microseconds to seconds cover the time-scales of dynamics of slow magnetic fluctuations in materials, such as thermally-

induced domain wall motion. (ii) Tens of nanoseconds to tens of picoseconds correspond to magnetic precessional frequencies, where we will study the dynamic response of nano-magnetic systems to nanosecond current, temperature and field pulses and (iii) pico-seconds to femto-seconds cover the time scales for energy and angular momentum transfer between orbital, spin and lattice degrees of freedom and can be used to probe the fundamental nature of phase transitions and the ultra-fast magnetization dynamics. (2) Interfacial phenomena in oxides We are studying the fundamental interfacial phenomena in complex oxide interfaces. This includes understanding the role of electric field effects in piezoelectric-ferromagnetic heterostructures and probing electronic reconstruction that occurs at oxide interfaces.

FY 2014 HIGHLIGHTS

(i) Effect of Electric fields on magnetization in Oxide films. Using resonant x-ray magnetic reflectometry, we measured the magnetization depth profile of an LSMO film as a function of electric field applied to the LSMO/PZT heterostructure. The polarization, its magnitude or direction, had no influence on the saturation magnetization of the ferromagnetic ordered film. However, in the absence of a magnetic field, the remnant magnetization and ferromagnetic thickness of the LSMO film decreased when the electric polarization of the PZT film promoted accumulation of hole-charge at the LSMO/PZT interface. These results are consistent with a picture that hole-doping induces weak ($< 6 \times 10^5$ erg/cm³) anti-ferromagnetic exchange between Mn⁴⁺ at the LSMO/PZT interface and nearest neighbor Mn moments. Tuning of Mn valence at an interface with electric potential applied to a ferroelectric may be a new route to control of interface magnetism. (ii) Magnetic vortex dynamics The dynamic annihilation of magnetic vortices was studied on a series of samples consisting from Permalloy (Ni₈₀Fe₂₀) disks with diameters ranging from 250 nm to 2500 nm and thicknesses from 20 nm to 50 nm. Magnetic field pulses were applied to the disks. The magnetization in the disks was imaged by the full-field transmission soft x-ray microscope at the Advanced Light Source in Berkeley, CA. These experiments allowed us to construct a pulse rise time – pulse amplitude phase diagram of successful vortex annihilation. We are able to distinguish three distinct regions: (1) a region of low pulse amplitude and long rise time, where the vortex core was not expelled out of the disk and gyrated freely in the disk with an unchanged polarity (2) a region of intermediate pulse amplitude and intermediate rise time, where the pulse parameters were sufficient to expel the vortex core out of the disk, and finally (3) a region of short rise time and high amplitude where circulation switching was not successful. (iii) Phase transitions in FeRh films: We used a suite of characterization techniques to characterize the nature of the antiferromagnetic-ferromagnetic phase transition in FeRh films and nanostructures including the critical behavior of the domain formation and the role of exchange. (iv) Skyrmion formation in Fe/Gd multilayers: We have mapped the magnetic field-temperature phase diagram of skyrmion lattice formation in Fe/Gd superlattices.

DOE National Laboratories

Impact of Dynamic Instabilities and Microstructure on Energy Materials

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Funding: \$1,623,000 (2014)

PROGRAM SCOPE

The goal of this project is to advance our fundamental understanding of how dynamic lattice instabilities interact with local microstructure to control the temperature-dependent physical properties of advanced materials. This knowledge is needed to accelerate the predictive discovery of energy materials under realistic operating conditions such as finite temperature. Issues of nonlinear lattice vibrations, phase competition and broken static symmetry play critical, but often unknown, roles in determining materials properties. This research will integrate state-of-the-art neutron and synchrotron x-ray scattering methods with first-principles computational techniques to obtain new scientific insights. In particular, research thrusts will focus on fundamental studies of technologically-important model materials including: localized dynamic instabilities in relaxor ferroelectrics and frustrated “strain glasses”; the role of anharmonic phonons in controlling phase competition in metal-insulator materials; and the interaction of ferroelectric instabilities with external fields. A common scientific hypothesis in the research is that strong lattice anharmonicity can be intentionally tuned to produce greatly enhanced physical responses. In addition, inhomogeneous nanostructures such as chemical order, precipitates and strains can be fashioned for further synergistic enhancements. Effectively exploiting instabilities and inhomogeneities in complex materials will require both detailed experimental characterization and fundamental understanding of how interactions drive physical properties. This project directly addresses these needs, and thus supports the DOE BES mission to provide the understanding needed to enable discovery breakthroughs in functional energy materials. The research will establish critical connections linking lattice dynamics and microstructure with first-principles theories to enable the prediction of enhanced materials.

FY 2014 HIGHLIGHTS

(1) Determined the origin of anomalous spectral lineshapes of highly-anharmonic ferroelectric soft-modes in PbTe, based on first-principles simulations of the phonon self-energy. This discovery offers new insights into the role of three-phonon scattering in phase-space in enhancing anharmonicity, to improve thermoelectric performance. (2) Established systematics of diffuse scattering from nanoscale self-ordering in AgSbTe₂ thermoelectrics, using a combination of synchrotron x-ray scattering, neutron scattering, and electron microscopy. These results show the importance of short-range ordering in scattering phonons and suppressing thermal conductivity. (3) Investigated the impact of lattice dynamics on the metal-insulator phase transition in vanadium dioxide by combining comprehensive neutron and x-ray scattering studies with large-scale, first-principles molecular dynamics calculations. Studies revealed that soft (low-energy), anharmonic phonons provide the entropy that overcomes the electronic energy to stabilize the metallic phase of VO₂ above room temperature. Research published in Nature, November 2014. (4) Discovered how phonon localization drives the formation of ferro- and anti-ferroelectric polar nanoregions (PNRs) in relaxor ferroelectric materials PMN-PT and PZN-PT. The idea is being extended to related systems to investigate if this phonon localization mechanism is more generic. (5) Discovered a phonon avoided crossing of PNRs in PZN-PT and PMN-PT relaxor-based ferroelectrics that induces a dynamic instability in the structure. We hypothesize that this instability is responsible for the giant electromechanical coupling observed in these materials near the morphotropic phase boundary. (6) Installed Pilatus hybrid pixel 2D array detector on our laboratory x-ray system, developed software for diffuse scattering analysis, and used in studies of Pb(Zr,Nb)O₃-PbTiO₃ relaxor ferroelectrics.

EARLY CAREER: Multiphase Soft Colloids: From Fundamentals to Application of Energy Sustainability

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Funding: \$500,000 (2014)

PROGRAM SCOPE

Multiphase soft colloids are synthetic macromolecules that possess at least two different types of functional groups located at the particle periphery. This class of materials represents a unique microscopic building block for designing bulk materials that perform multiple functions simultaneously. Their structural heterogeneity establishes interactions between colloidal particles that are directional in nature, introducing new functionality. Their complex nature must be understood in order to control the spatial arrangement of these particles to produce optimized macroscopic morphologies for functional devices. Thus, the overarching goal is to develop a fundamental understanding of the physical processes occurring on the nanometer length scale that are critical for the molecular-level design of these systems. Two specific aims form the basis of the proposed research: The first seeks to understand the microscopic interaction mechanisms giving rise to spatial organization on the length scale from that of an individual colloid to collective phase behavior. The second aim focuses the relationship between dynamics and structure that give rise to equilibrium phase behavior. Underpinned by specific tailored synthesis, these two specific aims provide the critical link between the bulk properties and the microscopic features of their precursor solution state. Emphasis is placed on understanding and controlling the anisotropic inter-particle interactions which determine structural organization in the solution and ultimately in their solid functional forms. A combination of the research capabilities of ORNL are employed to study the structure and dynamics of these materials. Isotopically labeled materials highlight the structural and dynamical signatures of neutron scattering, and computer simulations will be performed to provide a unified basis for interpreting the scattering measurements and to give deeper insight into the microscopic behavior of these soft colloids.

FY 2014 HIGHLIGHTS

(1) Structure and Dynamics of Soft Colloids Neutron scattering experiments revealed the existence of the crossover between the two dynamical degrees of freedom well below the overlap concentration. The concentration, at which the inter-molecular collision time is equal to the intra-molecular relaxation time, is defined as the dynamical crossover point. This important discovery discriminates the dilute regime where the inter- and intra-molecular dynamical processes can be fully decoupled. Moreover, we developed two new approaches to analyze the scattering data, and found the continuous desolvation of soft colloids below and beyond the overlap density due to increasing the concentration. Furthermore, to understand the effect of the associated solvent molecules on colloidal structure, we developed the scattering function of star polymers with the excluded volume effect, which shows quantitative agreement with experiment. Based on the same theoretical framework, we also developed a scattering function for polymer-colloid conjugates. (2) Phase Transition and Dynamics of Non-Centrosymmetric Nanoparticles We developed the scattering function for yolk-shell nanoparticles, a category of functional materials with a mobile core in a hollow shell. It facilitates the investigation of these novel materials

using scattering. We further predicted the dynamics of yolk-shell particles using Brownian dynamics simulation and generalized Langevin equation theory. Moreover, we studied the phase transition of another type of non-centrosymmetric particles, shifted charge colloids, using simulation. We discovered a liquid-to-crystal transition at a much lower concentration than centro-charged colloids. We also found that the system undergoes a continuous disorder-to-order transition with respect to the charge orientation. These investigations have provided critical information for the practical applications of these novel materials.

EARLY CAREER: Quasiparticle Couplings in Transport of Heat, Charge, and Spin for Novel Energy Materials

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Sr. Investigator(s):
Students: 0 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding: \$500,000 (2014)

PROGRAM SCOPE

Understanding the microscopic processes involved in the transport and conversion of energy from the atomic scale to the mesoscale is critical for the development of next-generation energy materials. The coupling of heat and charge transport is at the heart of thermoelectrics research and thermal engineering, enabling practical devices for “waste-heat harvesting” and heat pumping. At a microscopic level, this coupling results from interactions of phonons with other phonons owing to anharmonicity (phonon-phonon interaction, PPI), or with charge carriers (electron-phonon interaction, EPI). An additional and exciting dimension to these interactions has arisen from the recent discovery of the spin-Seebeck effect (SSE), whereby the interplay of phonons and magnons can link thermal and magnetic transport. Lack of detailed knowledge about quasiparticle couplings is impeding a full microscopic understanding of thermoelectrics and slowing the development of novel SSE devices. However, progress has recently been made, both experimentally and theoretically, in probing and understanding microscopic processes that determine the phonon propagation (scattering rates and mean-free-paths). Neutron and x-ray scattering techniques provide powerful microscopic insights that are key to rationalizing bulk transport measurements. In addition, developments in first-principles simulations enable the computation of phonon scattering rates from anharmonicity, and from electron-phonon coupling. This project uses state-of-the-art scattering experiments, complemented by transport measurements, computer simulations, and sample synthesis, and encompasses a broad range of materials for energy applications, including thermoelectrics and spin-Seebeck systems. Insights gained from this research program will directly impact technological approaches to control microscopic processes for energy harvesting and information processing.

FY 2014 HIGHLIGHTS

[This Early Career Award project was started in Q3 2014] (1) We have elucidated the origins of strongly anisotropic thermal transport in thermoelectric compound $\text{MnSi}_{1.75-x}$ (higher-manganese-silicide HMS). These compounds crystallize in a highly-anisotropic Nowotny chimney-ladder structure which leads to low-lying optical modes and “diffusion” transport, and unusual phonon transport. A manuscript is under review in Nature Communications. (2) Through inelastic neutron scattering (INS) measurements and

first-principles simulations, we have elucidated the origin of anomalous pair-distribution function peak shapes in rocksalt telluride thermoelectrics (SnTe / PbTe), establishing anharmonicity as the root of the effect (manuscript in press in Phys. Rev. B). (3) We investigated the phonon scattering mechanisms in single-crystals of thermoelectric FeSi doped with heavy elements Os, Ir. We predicted and observed the formation of resonance modes of heavy impurities, and showed that they interact strongly with acoustic modes, leading to the suppression in thermal conductivity and improvement in figure-of-merit (a manuscript is under review in Phys. Rev. B). (4) We have performed systematic measurements of the phonon dispersions and linewidths in the novel thermoelectric material SnSe with record-high efficiency. A publication is under preparation. (5) We have designed and built an ultrafast-optical time-domain thermoreflectance (TDTR) apparatus for the measurement of quasiparticle lifetimes and thermal conductivity in the time domain, in collaboration with Y. Ma and B. Doughty (CSD). (6) We have obtained beamtime at the SNS for INS measurements of coupled phonon-magnon heat transport in magnetic oxides of current interest as spin-Seebeck systems. We have also acquired and tested single-crystals for several compositions.

Correlations and Competition Between the Lattice, Electrons, and Magnetism

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Funding: \$1,264,000 (2014)

PROGRAM SCOPE

The properties of novel materials, such as high-temperature superconductors, charge/orbital ordering systems, and multiferroics, are all sensitively controlled by correlations and competition among the lattice, electronic, and magnetic degrees-of-freedom. A complete understanding of the interrelations between these systems and the necessary conditions for enhancing or tailoring desirable physical properties have been identified as a Grand Challenge to the scientific community. Neutron and x-ray scattering are powerful techniques that directly probe the structural, electronic, and magnetic aspects of complex ground states, phase transitions, and corresponding excitations. Within this FWP, the varied expertise of the PIs in different scattering methods is employed in a synergistic approach and systems are studied using a wide range of neutron and x-ray techniques. The experimental program is supported by a closely coupled effort in *ab initio* band structure calculations, theoretical modeling, and scattering simulations.

FY 2014 HIGHLIGHTS

Our inelastic neutron scattering measurements demonstrated that that the onset of superconductivity in $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ coincides with a crossover from well-defined spin waves to overdamped and diffusive excitations. [Phys. Rev. B 89 180503(R) (2014)] One of the keys to unconventional superconductivity lies in its proximity to an ordered antiferromagnetic (AFM) ground state. In $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ AFM order and superconductivity coexist and compete, permitting investigations of how the normal state spin

fluctuations provide the conditions for superconductivity to emerge. Measurements on the ARCS instrument at the SNS provided unambiguous evidence of the absence of magnetic fluctuations in the collapsed tetragonal (cT) phase of CaFe_2As_2 , demonstrating that the non-superconducting cT phase is also non-magnetic, consistent with the view that spin-fluctuations are a necessary ingredient for superconductivity in the iron pnictides. [Phys. Rev. Lett. 111, 227002 (2013)] The wide view in both Q and E available using TOF inelastic scattering on ARCS clearly demonstrates that all spin fluctuations are absent and, therefore, that the cT phase is non-magnetic. We have discovered that SrCo_2As_2 is close to an instability toward stripe-like AFM order, exhibiting steeply dispersing and quasi-two-dimensional paramagnetic excitations near the wavevector Q_{AFM} . [Phys. Rev. Lett. 111, 157001 (2013)] Dilute substitutions of Co for Fe in the AFe_2As_2 compounds (A = Ca, Ba, Sr) destabilizes the stripe-like AFM ordering and Co substitutions of only a few percent allows a superconducting ground state to emerge. Further Co substitutions (> 12% Co) lead to a complete suppression of both stripe-like spin fluctuations and superconductivity. The surprising re-emergence of stripe-like magnetic fluctuations in SrCo_2As_2 raises new questions regarding the origin of strip-like magnetic order in the iron pnictides.

Center for Accelerating Materials Modeling from SNS Data

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Funding: \$400,000 (2014)

PROGRAM SCOPE

Neutron scattering enables simultaneous measurement of structural and dynamic properties of materials from the atomic scale (0.1 nm, 0.1 ps) to the mesoscale (1 μm , 1 μs). These ranges are remarkably complementary to current capabilities of computational modeling, and the simplicity of the scattering cross section allows the prediction of neutron scattering data straight forwardly from atomic trajectories in a computer model. The Center for Accelerating Materials Modeling (CAMM) from SNS Data is accelerating the rate of scientific discovery by integrating modeling into all aspects of the experimental chain. We have developed a refinement loop using classical molecular dynamics (MD) as the modeling technique, in combination with quasielastic neutron scattering data from the BASIS instrument. We have successfully demonstrated the refinement of MD force-field parameters for LiCl, and the software tools developed have been subsequently used in several projects initiated by SNS users. The software tools developed to enable these studies are now made available to SNS users. Based on the demonstrated ability to perform force-field refinements from neutron data (e.g., experimental validated computational models), moving forward CAMM will focus on developing fundamental understanding of dynamics and transport in non-crystalline materials such as polymers, gels, composites, glasses, and colloids by using our integrated feedback with neutron scattering that has been established for validating and verifying force-fields to enable accurate simulations to explore the structure and dynamics.

FY 2014 HIGHLIGHTS

The goal of the Center of Accelerating Materials Modeling (CAMM) of SNS data is to close the gap between materials modeling and neutron scattering. CAMM teamed up with J. Budai and investigated the nature of the metal-to-insulator transition in VO₂ ultimately showing the metal phase is stabilized by lattice vibrations resulting in a paper appearing in Nature. Another CAMM project unraveled anharmonic lattice dynamics in SnTe and PbTe thermoelectrics using inelastic neutron scattering and finite temperature in the first-principled *ab initio* MD simulations. As part of efforts to integrate modeling and neutron scattering experiments in 'real time', a pilot experiment was carried out, that enabled instant access to high performance computing during an experiment on the HYSPEC instrument at ORNL. This allowed the team to run *ab initio* molecular dynamics simulations and use the results for decision making during the experiment. The results are currently being analyzed. The core tool developed by CAMM is a workflow allowing the refinement of input parameters of materials models based on neutron scattering data. Expanding on the initial demonstration of refining force constants from quasielastic neutron scattering data of LiCl in water, the work progressed to the refinement of nano-diamond RNA (work in progress). As part of outreach to SNS users, the current version of CAMM developed tools and the refinement framework has been made available including documentation, tutorials and the website <http://camm.ornl.gov>.

Neutron and X-Ray Scattering

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Daniel Phelan; Argonne National Laboratory
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Students: 2 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding: \$1,966,000 (2014)

PROGRAM SCOPE

The Neutron and X-ray Scattering Group investigates the structure and dynamics of bulk and interfacial strongly correlated systems with a particular focus on the role of phase competition in generating complex phenomena of interest in energy related materials, such as superconductivity, magnetism, thermoelectricity, etc. The latest advances in neutron and x-ray instrumentation at major DOE User facilities, in some cases developed by members of the group, allow us to investigate how materials respond on a range of length and time scales to competing interactions, so that we can learn to control emergent behavior in energy-related materials. Phase competition can generate or enhance material functionality, but it is extremely challenging to characterize fluctuations in the competing order, whether in bulk disordered materials or artificial heterostructures. Our goal is to utilize efficient techniques that we have been developing for measuring nanoscale phase fluctuations, both static and dynamic, to enable the rational design of new materials for energy within the Materials Science Division.

FY 2014 HIGHLIGHTS

A detailed investigation of the phase diagram of hole-doped $\text{Ba}_{1-x}\text{Na}_x\text{Fe}_2\text{As}_2$ by high resolution neutron powder diffraction revealed the existence of a novel state, a magnetic phase that restores tetragonal symmetry. Such a tetragonal, magnetic phase is predicted by spin-nematic theories, showing that nematic order in iron-based superconductors is driven by magnetic, rather than orbital, interactions. High resolution neutron powder diffraction was used to study in detail the structural and magnetic transitions in the hole doped and phosphor substituted $\text{Ba}_{1-x}\text{Na}_x\text{Fe}_2\text{As}_2$ and $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$. We find that in both cases the structural and magnetic transitions are coincident and weakly first order, but that the lattice anomaly in the P-substituted compounds is different than in the hole doped systems due to different evolution in the lattice component in the electronic ordering as function of doping. Polarized neutron reflectivity studies, combined with X-ray magnetic circular dichroism (XMCD) and theoretical modeling, reveal a strong effect of interface-induced magnetization on the temperature dependent transport properties of magnetic tunnel junctions consisting of ferromagnetic manganite $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ and insulating cuprate $\text{PrBa}_2\text{Cu}_3\text{O}_7$. These results provide evidence for a novel emergent spin-filter functionality not previously considered, and are of significant interest for both basic research and spintronics applications. Utilizing polarized neutron reflectometry and XMCD we demonstrated a reversible, voltage-driven magnetization switching without assistance from a magnetic field in a heterostructure consisting of an insulating copper oxide and a ferromagnetic manganite oxide and we show that the observed unusual magneto-transport behavior results from a novel form of magnetoelectric coupling arising from orbital reconstruction at the interface between these two strongly correlated oxides.

National School for Neutron and X-ray Scattering

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Students: 0 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding: \$232,000 (2014)

PROGRAM SCOPE

DOE is the leading organization in the United States involved in the design, construction, and operation of large-scale facilities for producing high-intensity neutron and x-ray beams for scientific research. A critical factor for making the most effective use of these facilities is educating the U. S. scientific user community in the potential of the wide array of measurement techniques available at these sources. Providing basic education in how neutron and x-ray scattering techniques can be applied to provide atomic scale information relevant to a variety of scientific disciplines is essential not only to the current users of these facilities, but even more so for graduate students who will form the next generation of scientists conducting experiments at the existing and future sources. The annual National School on Neutron and X-ray Scattering (NXS), jointly hosted by Argonne National Laboratory (ANL) and Oak Ridge National Laboratory (ORNL), has been extremely successful in fulfilling this purpose. This school distinguishes itself from other more topical schools in the United States by providing a broad grounding in the fundamentals of both neutron and x-ray scattering techniques, emphasizing the complementary nature of these structural probes. The NXS School offers, primarily to graduate students from North American Institutions, a comprehensive introduction to the underlying theory and the experimental

techniques that are available at major neutron and x-ray scattering facilities, especially in the United States. The students receive lectures from leading experts in the field. Furthermore, a key component of the school is the hands-on training provided using instruments at the Advanced Photon Source (ANL), the High Flux Isotope Reactor (ORNL) and Spallation Neutron Source (ORNL).

FY 2014 HIGHLIGHTS

The 16th National School on Neutron and X-ray Scattering was held from June 14-28, 2014. Out of 201 applicants, 66 participants were selected to attend, of which 60 were funded by this FWP. The participants spent the first week at Argonne National Laboratory and then transferred to Oak Ridge Laboratory on June 21, 2014 for the remaining period. Besides receiving a comprehensive course in the fundamentals of neutron and x-ray scattering theory and the associated techniques through lectures, in the afternoons, in groups of four, participants performed three or four synchrotron x-ray and four neutron scattering experiments. On the final day, each group of participants gave a 10-minute presentation, describing one of the experiments they had participated in. Overall, the feedback from the participants, as monitored by an extensive survey, is very positive, as has been the case for previous years. Lecture notes and videos have been made available through the school's websites (<http://neutrons.ornl.gov/nxs/2014/> and <http://www1.aps.anl.gov/nx>).

Complex Electronic Materials

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Roman Movshovich; Los Alamos National Laboratory
Students: 4 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding: \$1,746,000 (2014)

PROGRAM SCOPE

Complex electronic behaviors are most pronounced near magnetic/non-magnetic and metal/insulator boundaries in correlated materials and become particularly poorly understood as these boundaries are tuned to absolute zero temperature, i.e., to a quantum-critical point (QCP). With typically small characteristic energy scales, states of strongly correlated intermetallic compounds based principally on Ce, Yb, U and Pu can be tuned to these interesting boundaries with rather modest changes in a control parameter. The goal of this project is to develop an understanding of complex electronic materials and phenomena by discovering new examples of these and related materials that reveal both new states of electronic matter and the essential physics underlying their complex and collective states. Knowledge gained from studying correlated f-electron materials in parallel with technologically important d-electron materials provides a broad perspective necessary to guide the development of a microscopic theory of complex electronic materials. Success in this project of discovering new physics through new materials requires integration of materials preparation, in single crystal form where possible, with a necessarily broad suite of characterization techniques that probe static and dynamic degrees-of-

freedom and their interactions on multiple length and time scales. Our approach is two-fold: one of initial exploratory research on new materials and phenomena and a second of in-depth investigations. At the exploratory stage, structure, transport, magnetic and thermodynamic measurements, often at very low temperatures, high pressures and high magnetic fields, are sufficient to identify new states that deserve more detailed study by various spin and charge spectroscopies, particularly neutron scattering, nuclear quadrupole/magnetic resonance and photoemission.

FY 2014 HIGHLIGHTS

(1) We have studied the case of Cd-doped CeCoIn_5 , where Cd doping suppresses superconductivity and induces magnetic order. Specific heat, electrical resistivity and NMR measurements as a function of pressure find that pressure globally reverses the effect of Cd-doping, suppressing magnetic order and inducing bulk superconductivity with nearly the same T_c as in undoped CeCoIn_5 , but signatures of quantum criticality are absent. An analysis of these experiments reveals the formation of static 'droplets' of magnetism around the Cd-dopants that prevent the reappearance of conventional signatures of quantum criticality but induce a heterogeneous electronic state. (2) CeRhIn_5 , isostructural with CeCoIn_5 , is an antiferromagnet at atmospheric pressure but becomes superconducting under pressure with a maximum T_c at its QCP. We have used high-resolution neutron spectroscopy experiments to determine its complete spin-wave spectrum at ambient pressure. (3) Our inelastic neutron scattering measurements on a crystal of Pd-doped CeNi_2Ge_2 near its magnetic quantum critical point (QCP) demonstrate the role of disorder in assessing a QCP. (4) By growing very high quality crystals of URu_2Si_2 , we have enabled substantial progress on the nature of 'Hidden Order'.

Neutron Scattering

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Students: 1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding: \$2,388,000 (2014)

PROGRAM SCOPE

This program is organized around the challenge of understanding the antiferromagnetic spin correlations characteristic of high-temperature superconductors, with particular focus on systems such as copper oxides and the iron-based superconductors. The main experimental tools are neutron scattering and high-energy x-ray diffraction, with experiments performed at the best facilities in the U.S. and abroad. Problems addressed include: doping of correlated insulators, self-organized spin and charge inhomogeneities (such as stripes), electron-phonon coupling, spin dynamics, quantum magnetism in low-dimensional systems, and the impact of disorder. Growth of suitable single-crystal samples is an essential part of the program, with complementary characterizations performed in collaboration with other Brookhaven groups, especially at the National Synchrotron Light Source. There are also close interactions with the Center for Emergent Superconductivity, an Energy Frontier Research Center. This program leads the Instrument Development Team for HYSPEC, an inelastic spectrometer with

polarization analysis, now operating at the Spallation Neutron Source; it also participates in the US-Japan Cooperative Program on Neutron Scattering, which has partial access to the cold-neutron triple-axis spectrometer at the High Flux Isotope Reactor. The BNL-NIST Alliance involves collaborative efforts at the National Institute of Standards and Technology's Center for Neutron Research.

FY 2014 HIGHLIGHTS

Progress has been made in characterizing the magnetic correlations associated with superconductivity in the system Fe(Te,Se). In a study of the non-superconducting “parent” material Fe_{1+y}Te , a first-order ferro-orbital ordering transition has been identified and characterized by neutron scattering. In superconducting Fe(Te,Se), we have observed that substitution of Ni or Cu for Fe causes a suppression of the superconductivity but has little impact on the weight of low-energy antiferromagnetic correlations. For copper-oxide superconductors, our focus has been on the role of charge and spin correlations. A surprising time-reversal-symmetry breaking effect has been detected in the charge-stripe phase of $\text{La}_{1.875}\text{Ba}_{0.125}\text{CuO}_4$ through measurements of the polar Kerr effect. Crystals of underdoped $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ were prepared, enabling scanning tunneling microscopy and x-ray scattering studies of charge order. Competing charge, spin, and superconducting orders in $\text{YBa}_2\text{Cu}_3\text{O}_y$ have been characterized with the help of x-ray scattering. In the compound $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$, which is isostructural with superconductors, the fluctuations of charge stripes have been detected directly for the first time, by inelastic neutron scattering.

Physical Behavior of Materials

Institutions Receiving Grants

Magnetocaloric and Multifunctional Magnetic Materials

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Funding: \$199,999 (2014)

PROGRAM SCOPE

In this collaborative effort between Louisiana State University and Southern Illinois University, a comprehensive study is being conducted on a select group of materials that undergo magnetostructural phase transitions, and exhibit magnetocaloric and multifunctional phenomena. These systems include those based on the Heusler alloys $\text{Ni}_{50}\text{Mn}_{35}\text{In}_{15}$ and $\text{Ni}_{2-x}\text{Co}(\text{Mn}/\text{Al})$, and on the orthorhombic compounds MnT_x ($T=\text{Ni}, \text{Co}, \text{Cu}$ and $X=\text{Si}, \text{Ge}$). Investigations will also be carried out on the properties of magnetocaloric and multifunctional materials in thin film and nanocomposites forms in order to understand scale-size effects; the properties of these systems can vary greatly from those of the bulk. The detailed objectives of this project are the following: (i) To understand the effects of compositional variations and isoelectronic vacancies on the phase transitions and physical properties of $\text{Ni}_{50}\text{Mn}_{50-x}\text{In}_x$ and $\text{Ni}_{2-x}\text{Co}_x(\text{Mn}, \text{Al})$ Heusler alloys; (ii) to develop new metamagnets MnT_x and understand the underlying physics of the phase transitions in these systems; and (iii) to grow Heusler alloy and MnT_x thin films using pulsed laser deposition, and understand the ramifications of size-scale effects on the phase transitions and physical properties (including magnetocaloric effects). The potential scientific outcomes include: (i) the development of new magnetocaloric and multifunctional materials; (ii) a deeper understanding of the physics of the phase transitions responsible for magnetocaloric and multifunctional behaviors; and (iii) the discovery of new physical phenomena in thin films and nanocomposites materials. The discovery of a practical and effective magnetic refrigeration material would eventually lead to more efficient cooling systems. The impact of this could be profound: it would be one step towards energy independence, as this is one of our most energy-demanding technologies.

FY 2014 HIGHLIGHTS

The first highlight is our study on hydrostatic pressure-induced enhancements of the magnetocaloric effect in bulk $(\text{MnNiSi})_{1-x}(\text{MnFeGe})_x$. We observed a remarkable decrease of the structural transition temperature of MnNiSi from 1200 to < 300 K by chemically alloying it with MnFeGe , resulting in the coupling of the magnetic and structural transitions, and leading to a large magnetocaloric effect near room temperature. Application of low hydrostatic pressures (~ 2.4 kbar) led to an extraordinary enhancement of the isothermal entropy change from $-\Delta S = 44$ to 89 J/kg K at ambient and 2.4 kbar applied pressures, respectively, for a field change of $\Delta B = 5$ T. This was associated with a large relative volume change of about 7% with $P = 2.4$ kbar. (Phys. Rev. B 91, 020401(R) (2015) (Editor's Suggestion). The second highlight regards the isostructural alloying of two compounds with extremely different magnetic and thermo-structural properties, resulting in a new system, $(\text{MnNiSi})_{1-x}(\text{FeCoGe})_x$, that

exhibits extraordinary magnetocaloric properties with an acute sensitivity to applied hydrostatic pressure. Application of pressure shifts the first-order phase transition to lower temperature ($\Delta T = -41$ K with $P = 3.43$ kbar) but preserves the giant value of isothermal entropy change ($-\Delta S_{\max} = 143.7$ J/kg K for a field change of $\Delta B = 5$ T). (Submitted to Applied Physics Letters, Patent Application Number 62/062,0901, filed 18 July (2014)). The patent also applies to $(\text{MnNiSi})_{1-x}(\text{MnFeGe})_x$. Finally, we discovered an asymmetric switching behavior in the low-field magnetoresistance of the bulk metamagnetic Heusler alloy, $\text{Ni}_{50}\text{Mn}_{35}\text{In}_{15-x}\text{B}_x$. This novel physical phenomenon resembles a large asymmetric switching-like magnetoresistance at low applied fields. A thermally-activated isothermal forward metamagnetic transition with a signature of a pronounced time-dependent relaxation was observed, whereas the reverse metamagnetic transition exhibited the usual thermal behavior. (Phys. Rev. B 90, 064412 (2014)).

Electrochemical Potential Control of Mesophotonic Structures

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Funding: \$200,000 (2014)

PROGRAM SCOPE

Our project has two broad objectives: 1) to understand how electrochemical potential modulation gives rise to striking changes in the optical properties of materials in the transition from plasmonic to dielectric behavior and 2) to understand how resonant and nonresonant optical excitation of nanostructures alters the electrochemical potential state of photonic materials. We are investigating electrochemical potential control in nanophotonic structures by external gating in i) composite conducting oxide/metallic resonant nanostructures, ii) graphene nanostructures, and iii) hybrid graphene/metallic nanostructures. Variation of the electrochemical potential enables an extremely large modulation of the refractive index ($\Delta n \sim 1$) in conducting oxides at visible and infrared frequencies, and gives rise to interesting tunable resonant phenomena. We are also investigating electrochemical potential control of resonant plasmon excitation in arrays of graphene nanostructures with critical dimensions in the 10-100 nm range. Tunable resonant mid-infrared absorption features due to transverse and longitudinal plasmonic metamaterial resonances are achievable, as are coupling of plasmons to localized phonon polariton modes in the underlying substrate. While graphene metastructures have relatively low quality factors Q , their extremely small mode volumes V and hence Q/V have potential to enable very large Purcell factors. By applying large potential modulations in ultrasmall (< 10 nm) resonators we will explore the possibility of realizing plasmonic graphene structures at infrared wavelengths that can couple to and dramatically modify spontaneous emission and scattering in quantum dots and atomic emitters.

FY 2014 HIGHLIGHTS

(1) Plasmoelectric Potentials in Metal Nanostructures: We introduced a new method using an all-metal geometry, based on the plasmon resonance in metal nanostructures. In arrays of Au nanoparticles on an indium-tin-oxide substrate and arrays of 100-nm-diameter holes in 20-nm-thick Au films on a glass substrate, we showed negative and positive surface potentials during monochromatic irradiation at wavelengths below or above the plasmon resonance respectively. We observed plasmoelectric surface

potentials as large as 100 mV under 100 mW/cm² illumination. Plasmoelectric devices may enable development of entirely new types of all-metal optoelectronic devices that can convert light into electrical energy. (2) Tunable Large Resonant Absorption in a Midinfrared Graphene Salisbury Screen: The optical absorption properties of periodically patterned graphene plasmonic resonators were studied experimentally as the graphene sheet is placed near a metallic reflector. By varying the size and carrier density of the graphene, the parameters for achieving a surface impedance closely matched to freespace ($Z_0 = 377 \Omega$) are determined and shown to result in 24.5% total optical absorption in the graphene sheet. Theoretical analysis shows that complete absorption is achievable with higher doping or lower loss. This geometry, known as a Salisbury screen, provides an efficient means of light coupling to the highly confined graphene plasmonic modes for future optoelectronic applications. (3) Electronic Modulation of Infrared Radiation in Graphene Plasmonic Resonators: We experimentally demonstrated tunable electronic control of blackbody emission from graphene plasmonic resonators on a silicon nitride substrate. We showed that the graphene resonators produce antenna-coupled blackbody radiation, manifest as narrow spectral emission peaks in the mid-IR. By continuously varying the nanoresonator carrier density, the frequency and intensity of these spectral features can be modulated.

Nanocrystal-Based Diodes for Solar to Electric Energy Conversion

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Students: 1 Postdoctoral Fellow(s), 2 Graduate(s), 1 Undergraduate(s)

Funding: \$51,929 (2014)

The University of Pittsburgh part of this project is listed separately under Principal Investigator: David Waldeck

PROGRAM SCOPE

We are exploring charge transfer in nanoparticle-based materials that promise to provide a systematic and modular approach to creating a new generation of solar energy conversion devices. In bulk heterojunction device architectures, sets of semiconductor nanoparticles self-organize at the interface of two photoconductive polymer phases. Such structures have the key beneficial features of being produced by self-assembly processes, in which the surface functional groups direct the nanoparticles and polymer interfaces in a composite material, and they are composed of modular components (nanoparticles, linkers, and conjugated polymers), which can be optimized separately. Our goal is to identify properties of the charge transfer elements and their assemblies that will allow such devices to capture the entire available range of solar irradiance, to efficiently transduce the absorbed energy to separated charges, and to form by self-assembly into a robust structure. While much is known about the properties of nanoparticles (NPs) and conjugated polymers (CPs) as separate entities, much less is known concerning their property evolution as they assemble into functional structures. Indeed, one's ability to predict and control the optical, electronic, and electron transfer characteristics at NP/NP and NP/CP interfaces, from knowledge of their individual electronic properties, is in an early stage of development. For example, the charge transfer efficiency of any photo-electric device depends critically on the energy level alignment of its components, relative to each other and relative to the system's Fermi-level. The project team is working on the design, synthesis, and characterization of linked-nanoparticle and conjugated polymer assemblies, which will act as the charge separation "engines" in new generation solar cells.

FY 2014 HIGHLIGHTS

The through-bond and through-space electronic couplings between two semiconducting nanoparticles (NPs) in a NP-bridge-NP system was analyzed theoretically using tight-binding electronic structure methods. We are exploring how the NP radius, solvent environment and molecular linkage influence the magnitude and distance dependence of the couplings. As the radii of the NPs increase, the through-bond and through-space couplings decrease at distinctive rates. We have identified crossover radius for fixed linker distances at which the strengths of the through-space and through-bond couplings will dominate. As such, we have identified regimes in which linker structure would significantly influence the charge separation rates and their distance dependences, and regimes in which the charge separation kinetics would be weakly structure dependent. We are using the results of these studies, as well as analysis of how surface modifications of NPs may polarize donor/acceptor states to define transport kinetic mechanisms and control strategies for NP-to-NP photoinduced charge separation.

Coherent Control of Spin States in Organic Electronic Devices - Manipulation of Electron-spin Interactions for Organic Electronics and Spintronics

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Students: 3 Postdoctoral Fellow(s), 3 Graduate(s), 1 Undergraduate(s)
Funding: \$185,000 (2014)

PROGRAM SCOPE

This project focuses on using spin-dependent electronic transitions in organic conductors and semiconductors for the study of spin-spin interactions of charge carriers. Spin-spin interactions can profoundly determine the nature of spin-dependent recombination processes which in turn can strongly affect electrical, optical, and magnetic materials properties of organic semiconductors. The research plan of this project encompasses three work areas: (i) the study of spin coupling (spin-dipolar and spin-exchange, spin-orbit, hyperfine interactions) in various organic semiconductor materials including pi-conjugated polymers with various degrees of local hyperfine field strengths such as different polyfluorene- and poly(p-phenylene vinylene)-derivatives (PPV), polystyrene sulfonate doped poly(3,4-ethylenedioxythiophene) (PEDOT:PSS) as well as new, recently synthesized materials; (ii) the exploration of electric field-control schemes of spin-exchange and -dipolar interactions between charge carriers in pi-conjugated polymers. This research activity is motivated by the prospect that an electric field dependence of spin-interactions could offer new routes for spin manipulation and thus new pathways for the control of spin-dependent macroscopic materials properties; (iii) the electrical detection of nuclear spins and hyperfine interactions and thus the question of how the nuclear spin-degree of freedom influences macroscopic magneto-optoelectronic materials properties of organic semiconductors.

FY 2014 HIGHLIGHTS

One important accomplishment of this project during fiscal year 2014 has been to experimentally verify that nuclear spin states of the omnipresent hydrogen in organic semiconductors play an important role

for the electronic and optoelectronic properties of these materials. The idea behind these experiments was to show that if proton spins affect a material's conductivity through influencing electron spins of spin-dependently recombining charge carriers as previously claimed in literature reports, then a nuclear magnetic resonance (NMR) manipulation of proton spins will cause a change in conductivity. The technical challenge of this experiment was to overcome the low polarization of proton ensembles at low magnetic fields and high temperatures. This problem was solved in two ways: First, by electrically measuring the effect of coherent nuclear spin motion on coherent electron spin motion through an electrically detected electron spin-echo envelope modulation (ESEEM) pulse scheme which projected Larmor oscillations of nuclear spins onto the electron-spin state of recombining charge carriers. By repeating these ESEEM experiments with the same polymer material (MEH-PPV) but substituted hydrogen isotopes where deuterium nuclei rather than protons were used on the 2-ethylhexyloxy side groups, it was demonstrated that the characteristic Larmor precession of the proton spins modulates the charge carrier spin echo decay. The second way to test nuclear spin control by electric currents was to directly observe current changes caused by application of nuclear magnetic resonance (NMR) to the hydrogen spins of a polymer. The electrical NMR resonance detection was achieved by using an electron-nuclear double resonance pulse sequence which selectively excited a highly spin-polarized nuclear spin subensemble. The detected NMR lines allowed for the determination of the strength and distribution of hyperfine couplings to charge carriers in the investigated material.

First Principles Prediction of Structure, Structure Selectivity, and Thermodynamics Stability Under Realistic Conditions

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Funding: \$220,000 (2014)

PROGRAM SCOPE

There has been considerable progress in the first principles prediction of materials properties through the development of new and more relevant algorithms, coupled to more accurate and robust quantum mechanical approximations. This has led to the emergence of several success stories in computational materials development and has highlighted the potential for *ab initio* computation as a virtual materials laboratory. More recently, high-throughput computing has shown that predictions can rapidly be scaled to tens of thousands of known and virtual compounds. In this project we tackle three important and interconnected components of computationally driven materials design: The prediction of crystal structure, the effect of particle size and environment on structure, and the rational determination of synthesis paths for metastable structures. The properties of a material derive from its structure; therefore the capability to predict which structures will form in a compound is a central problem of materials design and engineering. The most stable structure of a material is the one with the lowest (free) energy, a mathematically well-defined but difficult to solve optimization problem. Previously, we have combined data mining with density functional theory methods to develop a very efficient structure prediction tool, requiring typically only 10–15 energy evaluations to obtain the lowest energy structure. We now are extending this approach and data-mine the common substructures of crystal structures so that for a novel compound, the likely local atomic environments can be predicted. Coupled with crystal structure construction algorithms, such an approach will allow us to predict completely new structure

prototypes, enable the relation between structural environments, properties, and composition to be expressed more completely, and make it possible to extend our approach to non-periodic and low symmetry situations (such as surfaces).

FY 2014 HIGHLIGHTS

Our accomplishment this year involves the development of a distance semi-metric in compound space. The availability of large amounts of data generated by high-throughput computing or experimenting has generated interest in the application of machine learning techniques to materials science. Machine learning of materials behavior requires the use of feature vectors or descriptors that capture the essential compositional or structural information that is most likely to influence a property. While humans tend to use intuitive –and imprecise – ideas to evaluate whether two chemistries or crystal structures are the same, machine learning requires quantitative metrics to evaluate “similarity”. Rigorous structure descriptions including concepts such as unit cells and symmetry, but chemists and materials scientists often use more intuitive and less well-defined terminology such as local environment, coordination, and polyhedral connectivity, to explain the properties of a compound. Indeed, unit cells and symmetry vary discontinuously with small changes in the atomic coordinates, and therefore do not provide a good set of descriptors in which to understand or expand materials properties. We have developed a mathematical description of structure and chemistry that can be used to create a distance semi-metric between compounds. This allows us to rigorously define similarity between compounds, and we expect this formalism to form the basis for machine learning approaches in materials science. Our novel semi-metric captures both topological and chemical information of the local environment around atoms (i.e. an octahedral site formed by oxygen ions is different from one formed by metal atoms). We combine a distance metric in chemical space (the ionic similarity) and in topological space (the coordination similarity), and coarse-grain the environment observed in known compounds (e.g. as documented in the ICSD database.)

Spectrally-Tunable Far-Field Thermal Radiation Extraction from Micro and Nanostructures

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Funding:	\$480,000 (2014-2017)

PROGRAM SCOPE

The overall goal of this project is to explore a new approach towards radiative heat extraction from the near-field regime into the far-field regime that utilizes morphology-mediated thermal emission. Morphology-mediated global and local DOS engineering in photonic structures has already been successfully used to either enhance or inhibit light absorption, fluorescence rates, Raman scattering efficiency, and near-field energy transfer for applications in on-chip communications and sensing. However, the broadband nature of thermal emission and the temperature dependence on the occupancy of available states make engineering the electromagnetic potential for heat extraction much more challenging. To date, there has been no systematic attempt to harness the high LDOS of confined photon states to design cold thermal extractors as well as hot thermal emitters in the far field. Furthermore, the limits of radiative heat extraction via any generalized thermal extraction scheme have

never been estimated. The only exceptions are the far-field extraction through dielectric prisms and known theoretical results from the Mie theory for some low-dimensional emitters/absorbers. Therefore, this project seeks to develop a general understanding and specific design rules for morphology-mediated radiative heat extraction both theoretically and experimentally. In particular, mechanisms of manipulating far-field thermally-emitted photons via engineering of local electromagnetic potentials will be investigated. The limits of thermal radiation from (or via coupling to) micron and nanoscale structures into the far field will also be investigated. We will also explore new possibilities to convert low energy photons into high energy phonons via phonons in low-dimensional thermal absorbers/emitters. The feasibility and efficiency limits of the thermal up-conversion in the low-dimensional structures with spectrally-tailored LDOS characteristics will be assessed.

FY 2014 HIGHLIGHTS

We studied radiative heat transfer between thin films in the near-field and far-field regimes using the Rytov theory. By reducing the thickness of the emitter and the absorber, spectral selectivity for thermal emission and absorption was improved due to the photon confinement in analogy to the electron confinement in quantum wells. We applied this approach to thermophotovoltaic (TPV) systems to improve energy conversion efficiency. Using a realistic electrical model for the PV cell, we predicted a thermal-well TPV efficiency of 38.7% in the near-field regime (100nm gap separation) and 31.5% in the far-field regime for a Ge emitter at 1000K and a GaSb cell at 300K. We also studied via the generalized Mie theory radiative heat extraction using SiO₂ microspheres (acting as thermal dots) to reduce excess heating of illuminated metal nanoparticles. We show that hybrid metal-particle-thermal-dot structures enable two orders of magnitude enhancement of localized electric fields while simultaneously reducing dissipative heating of metal and enhancing thermal emission. These effects result in particles temperature reduction by 100-300K for the irradiance of 106 W/m². We also continued to experimentally characterize near-field radiative transfer using an AFM bilayer cantilever. Experimental configurations so far have been limited to either two parallel plates or a sphere and a plate. We developed and conducted the first experimental measurement of near-field radiative transfer between two spheres. SiO₂ microspheres with a diameter of 46 μm were used. Experimental results showed good agreement with theory for gaps wider than 200nm, and at smaller gaps, deviated from theory due to spheres roughness (RMS surface roughness ~40 nm and peak to peak ~200 nm). We also developed an atomistic approach based on nonequilibrium Green's function and microscopic Maxwell equations to describe the transition from phonon radiation in the far and near field to phonon heat conduction at contacts.

EARLY CAREER: Prediction of Thermal Transport Properties of Materials with Microstructural Complexity

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Funding: \$150,000 (2014)

PROGRAM SCOPE

This project focuses on overcoming the major obstacle standing in the way of progress in dynamic multiscale simulation, which is the lack of a concurrent atomistic-continuum method that allows elastic

waves, heat and defects to pass through the atomistic-continuum interface. The primary goal of this research is to establish a concurrent multiscale methodology that can overcome this obstacle and that can be used to simulate and optimize materials with microstructural complexity. In pursuit of this goal, we propose to reformulate the classical statistical mechanical theory of transport processes to unify atomistic and continuum descriptions of balance laws and recast the governing equations to facilitate coarse-scale finite element simulation of discontinuous materials behaviors. The proposed methodology will be tested through concurrent atomistic-continuum simulation of thermoelectric materials and comparing the mechanical and thermal transport properties of thermoelectric materials from simulations with those from experimental measurements. It is anticipated that this research will lead to a new mechanical theory of transport processes, a new simulation tool that provides a unified treatment for mechanical and thermal transport behavior, and a fundamental understanding of the effects of microstructure, interfaces, and defects on phonon transport processes in complex thermoelectric materials.

FY 2014 HIGHLIGHTS

Using stroboscopic X-ray topography, Shilo and Zolotoyabko in 2003 explicitly visualized the interactions between dislocations and surface acoustic phonons (~580MHz in frequency and ~6 μ m in wavelength). However, it is not yet possible in experiments to directly observe dislocation interactions with short- to medium-wavelength high-frequency (GHz) phonons. Atomistic simulations, on the other hand, are limited to very short length scales. Using the concurrent atomistic-continuum (CAC) method that we have been developing, we have explored the dynamic dislocation-phonon interaction process and demonstrated that CAC are capable of providing detailed information on dislocation interactions with phonons that have wavelength from nanometers to microns. The mean dislocation velocity is computed and the phonon drag coefficient on dislocation motions is predicted. During dislocation-phonon interaction processes, the energy transferred from the incident phonons has been quantified and local temperature rise is estimated. We have also identified the underlying physical nature associated with the phonon-drag mechanism: an atomic-scale “breathing mode” in which the separation between leading and trailing partial dislocations fluctuates with time in a quasi-periodic fashion.

Electrochemically-Driven Phase Transitions in Battery Storage Compounds

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Funding:	\$146,000 (2014)

PROGRAM SCOPE

Compounds of interest for ion storage in advanced batteries frequently exhibit phase transformations as the concentration of the working ion varies. Under the large electrochemical driving forces inherent to practical use, systems are often driven far from equilibrium. In this program a combined theoretical-experimental study is developing a predictive understanding of the interaction between materials composition, transformation strain, crystallite size and shape, and the electrochemical conditions driving the phase transition. Behaviors at the nanoscopic to mesoscopic scale under electrical overpotentials that vary in magnitude and with time are of special interest. The systems to be studied have

fundamental and practical interest, and include lithium and sodium transition metal olivines, $AMPO_4$ ($A = Li, Na; M = Fe, Mn, + \text{additives}$) exhibiting a wide range of transformation strains. Phase-field modeling of phase stability and transformation pathways is combined with operando experiments in which electrochemical titration is conducted simultaneously with characterization by synchrotron X-ray diffraction, neutron scattering, or transmission electron microscopy, using DOE facilities. Understanding of phase transformation pathways is expected to lead to new materials design concepts, and electrochemical duty cycles, that improve capacity utilization at high charge/discharge rates, control voltage and capacity hysteresis, and improve life by reducing cycling-induced mechanical fatigue.

FY 2014 HIGHLIGHTS

Nanoparticle olivine cathodes are the basis for large and growing class of high-power, long-life Li-ion batteries. The prototype in this family, $LiFePO_4$, has recently been shown to exist in binary lithiated/delithiated states at intermediate states of charge. Interestingly, the Mn-bearing version, $LiMn_yFe_{1-y}PO_4$, exhibits even higher rate capability as a lithium battery cathode than $LiFePO_4$ of comparable particle size. To gain insight into the cause(s) of this desirable performance, the electrochemically-driven phase transformation during battery charge and discharge of nanoscale $LiMn_{0.4}Fe_{0.6}PO_4$ of three different average particle sizes, 52, 106 and 152 nm, was investigated by operando synchrotron radiation powder X-ray diffraction. In stark contrast to the binary lithiation states of pure $LiFePO_4$ revealed in recent investigations, formation of metastable solid solutions covering a remarkable wide compositional range, including while in two-phase co-existence, are observed. Detailed analysis correlates this behavior with the existence of small elastic misfits between phases compared to either pure $LiFePO_4$ or $LiMnPO_4$. On the basis of time- and state-of-charge dependence of the olivine structure parameters, a coherent transformation mechanism is proposed. These findings illustrate a completely different phase transformation mode for pure well-ordered nanoscale olivines compared to the well-studied case of $LiFePO_4$. The results suggest that surprisingly large deviations from equilibrium under electrochemical driving force are not only possible but common, and inform the design of new battery materials.

Materials, Physics, and Nanostructures for Next Generation Spintronics

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Funding: \$190,000 (2014)

PROGRAM SCOPE

The research program focuses on various new spintronic phenomena, in particular pure spin current, its generation, detection, and exploitation. In contrast to a spin-polarized current, a pure spin current delivers the same spin angular momentum with fewer charge carriers thus generating less Joule heat. The situation is even more advantageous in ferromagnetic insulators, where there are no charge carriers, the magnons transmit the pure spin current with practically no heat dissipation. The few mechanisms that can generate a pure spin include spin Hall effect (SHE), spin pumping, non-local, and longitudinal spin Seebeck effect. Since a spin current cannot be directly detected by electric means, one employs other mechanisms, such as the inverse spin Hall effect (ISHE) in metals with strong spin-orbit

interaction to convert a pure spin current into a charge current or charge accumulation and be detected. We explore spin current injection into non-magnetic metals, ferromagnetic insulators, as well as ferromagnetic and antiferromagnetic materials. We devise methods to measure the spin Hall angle, which dictates the efficiency of charge/spin current conversion. We explore the physical phenomena that involve the interplay of charge, spin, and heat in the proximity of magnetic materials, as well as switching of nanomagnets by pure spin current using patterned nanostructure such as magnetic tunnel junctions.

FY 2014 HIGHLIGHTS

(1) A New Method for Self-Consistent Determination of Spin Hall Angle: Despite its importance, the reported values of spin Hall angle for a metal (e.g., Pt, Au, Ta, W), can vary by as much as two orders of magnitude. The disparity in the values of spin Hall angle is one of the most outstanding issues in spin current phenomena. We recently demonstrated a self-consistent method to determine spin Hall angle by employing a simple metal/ferromagnetic insulator structure and use thermally injected spin current from a ferromagnetic insulator into metals of different thicknesses and perform full spin current analyses of the ISHE voltage [Phys. Rev. B 89, 140407 (R), 2014]. (2) Physical Origins of the New Magnetoresistance in Pt/YIG: Recently, we have demonstrated a new type of magnetoresistance (MR) in Pt/YIG [Phys. Rev. Lett. 109, 107204, 2012]. As a nonmagnetic metal, Pt in isolation shows no discernible MR. In contrast, Pt on ferrimagnetic insulator YIG exhibits a sizable MR with characteristics different from all other known MR, including anisotropic MR (AMR), giant MR (GMR), and colossal MR (CMR). Spin Hall MR (SMR) due to spin/charge current conversion and magnetic proximity effect (MPE) have been proposed to account for the new MR. Our recent work [Phys. Rev. Lett 112, 236601 (2014).] shows that SMR has a small contribution mostly at low fields, whereas most of the new MR comes from MPE.

Extreme Thermoelectric Behavior in Low-Dimensional Oxide Conductors

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Funding: \$125,000 (2014)

PROGRAM SCOPE

The intellectual focus of this project is extreme thermoelectric behavior in bulk, low-dimensional oxide compounds. Two main foci: (1) materials with high Seebeck anisotropy in mutually perpendicular directions near room temperature, with potential for applications using the transverse Seebeck or Peltier effects, and (2) thermomagnetic studies (magneto-thermopower and Nernst) on $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$ (LiPB) at low temperature (to 0.3 K) to probe its superconducting and density-wave ground state. Figuring prominently in the proposed work were observations [Phys. Rev. Lett. 108, 056604 (2012)] revealing a giant Nernst coefficient in $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$ (LiPB) – among the largest known for metals (~450 $\mu\text{V}/\text{KT}$ at 20 K) and rivaling those of bismuth and graphite – and a thermomagnetic figure of merit $ZT \sim 0.5$ (at 30-50K and high magnetic field), a record in this temperature regime. A goal of this project is to answer remaining questions about the physics underlying this extreme thermomagnetic behavior of this compound and whether it might be made suitable for Ettingshausen cooling (i.e., improving ZT at a practical field scale). The research program involves substantial efforts to correlate physical properties

with structure and stoichiometry. The PI's X-ray scattering determinations of lattice constants and oxygen content analyses (energy or wavelength-dispersive analysis of x-rays) on individual crystals are complemented by materials synthesis (single crystals) and other characterization (neutron scattering, thermal expansion) provided by external collaborator Prof. John J. Neumeier (Montana State University).

FY 2014 HIGHLIGHTS

Research efforts during FY 2014 focused on (1) anisotropic transport measurements (electrical conductivity, Seebeck, and thermal conductivity) in the range 200K - 520K on the Mo oxide, $\text{Li}_{0.33}\text{MoO}_3$, and (2) low-T (to 0.3 K) magneto-transport measurements along the quasi-one-dimensional chains of LiPB in its field-suppressed superconducting state, and (3) a new parallel effort on the study of heat conduction in spin-chain and ladder compounds [e.g., CuSb_2O_6 , BiCu_2PO_6] to explore spin-phonon coupling and magnetic heat transport, potentially relevant to spin caloritronic applications. A new helium-3 probe with 5-T magnet was acquired just prior to the start of FY 2014 – this entailed several low-T runs to test the instrument and to calibrate low-T thermometry (RuO sensors) as functions of temperature and magnetic field. Briefly, these investigations have revealed: (1) very high Seebeck anisotropy and low thermal conductivity in $\text{Li}_{0.33}\text{MoO}_3$ near 300 K and x-ray evidence for a small increase in the b^* lattice constant (transverse to the layer stacking of the triclinic structure) upon cooling through a heretofore unexplained electronic transition near 360 K, (2) a very small effective Fermi temperature in the field-suppressed ground state of LiPB that offers new insight into the nature of its superconducting and competing density-wave orders, and (3) strong resonant spin-phonon scattering in the spin chain and ladder compounds noted above.

Phonon and Electron Transport in Pristine Two-Dimensional Layered Nanostructures and Heterostructures

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PROGRAM SCOPE

This project investigates thermal and thermoelectric transport in two-dimensional layered nanostructures and heterostructures. Although graphene is an ideal two-dimensional (2D) material that has enabled fundamental studies of unique low-dimensional physics and potential applications, its lack of an intrinsic band gap presents a challenge for the use of graphene in electronic and energy conversion devices. As a result, other 2D materials with different band gap values have begun to receive increasing attention. In addition, novel device concepts based on heterostructures composed of graphene and different 2D layered materials have emerged recently. The scope of our research includes the following specific topics: (1) Thermal Transport in Two-Dimensional Layered Nanostructures (a) Pristine Suspended Graphene, Hexagonal Boron Nitride, and Germanane (b) Phonon-Edge Scattering in 2D Nanoribbons (2) Thermal Transport in Two-Dimensional Layered Heterostructures (a) Cross-plane Phonon Transport (b) In-plane Phonon transport (3) Coupled Electron-Phonon Transport in Layered Heterostructure Devices (a) Single Tunnel Barriers (b) Field-effect Tunneling Transistors (c) Resonant

Tunnel Diodes (d) Thermionic Energy Conversion Devices. The main goal of this fundamental research effort is to gain new knowledge on the transport and conversion of energy carriers (phonons and electrons) in a new class of 2D materials with novel structures, functionalities, and properties. The structure-property relationships established in this project can serve as the basis for designing high-performance electronic devices and energy conversion devices employing these 2D materials.

FY 2014 HIGHLIGHTS

(1) Thermal Interface Conductance across a Graphene/Hexagonal Boron Nitride Heterojunction: During FY 2014, we reported the first measurement of the thermal transport across a graphene/hexagonal boron nitride (h-BN) interface by electrically heating the graphene and measuring the temperature difference between the graphene and BN using Raman spectroscopy. Because the temperature of the graphene and BN are measured optically, this approach enables nanometer resolution in the cross-plane direction. A temperature drop of 60K can be achieved across this junction at high electrical powers (14mW). Based on the temperature difference and the applied power data, we determine the thermal interface conductance of this junction to be 7.4×10^6 W/m²K, which is below the 10^7 - 10^8 W/m²K values previously reported for graphene/SiO₂ interface. (2) Thermoelectric/Thermionic Transport Across Graphene/Boron Nitride/Graphene Heterostructures: In addition to thermal transport, we also reported thermoelectric transport measurements across a graphene/hexagonal boron nitride (h-BN)/graphene heterostructure device. Using an AC lock-in technique, we are able to separate the thermoelectric contribution to the I-V characteristics of these important device structures. The temperature gradient is measured optically using Raman spectroscopy, which enables us to explore thermoelectric transport produced at material interfaces, across length scales of just 1-2 nm. Based on the observed thermoelectric voltage (ΔV) and temperature gradient (ΔT), a Seebeck coefficient of -99.3 $\mu V/K$ is ascertained for the heterostructure device. The obtained Seebeck coefficient can be useful for understanding the thermoelectric component in the cross-plane I-V behaviors of emerging 2D heterostructure devices. These results provide an approach to probing thermoelectric energy conversion in two-dimensional layered heterostructures.

Densely Aligned Graphene Nanoribbon Arrays and Bandgap Engineering

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Funding: \$136,796 (2014)

PROGRAM SCOPE

Graphene has attracted great interest for future electronics due to its high mobility and high thermal conductivity. However, a two-dimensional graphene sheet behaves like a metal, lacking a bandgap needed for the key devices components such as field effect transistors (FETs) in digital electronics. It has been shown that graphene nanoribbons (GNRs) with ~ 2 nm width can open up sufficient bandgaps and evolve into semiconductors to exhibit high on/off ratios useful for FETs. However, a challenging problem has been that, such ultra-narrow GNRs (~ 2 nm) are difficult to fabricate, especially for GNRs with smooth edges throughout the ribbon length. Despite high on/off ratios, these GNRs show very low mobility and low on-state conductance due to dominant scattering effects by imperfections and

disorders at the edges. Wider GNRs (>5 nm) show higher mobility, higher conductance but smaller bandgaps and low on/off ratios undesirable for FET applications. It is highly desirable to open up bandgaps in graphene or increase the bandgaps in wide GNRs to afford graphene based semiconductors for high performance (high on-state current and high on/off ratio) electronics. It has been shown theoretically that uniaxial strains can be applied to a GNR to engineer its bandgap. The underlying physics is as follows. Under uniaxial strain of several percent, though the position of cutting lines (allowed k states) for GNRs is unchanged relatively to the Brillouin zone for graphene, the Dirac point (where $E_g=0$) starts to move away from the corners of the distorted Brillouin zone due to stretched C-C bonds, leading to an increase in the bandgap of armchair GNRs by up to 50% of its original bandgap (i.e. bandgap at zero strain). The objectives of this work are to (1) fabricate high-density aligned graphene nanoribbon (GNR) arrays with GNR widths of 5-20 nm and pitch of <50 nm by using diblock copolymer lithography, (2) develop anisotropic etching of graphene capable of producing GNR edges.

FY 2014 HIGHLIGHTS

In year 2014 we succeeded in strain engineering of graphene nanoribbons, and a paper was published in *Advanced Materials*. Until this work, there has been a lack of reported experimental investigations into creating mechanical strains in GNRs, as well as into its effects on their material properties. In our work, uniaxial strains (0%-6%) were applied to individual GNRs with highly smooth edges by atomic force microscopy (AFM) manipulation and the strain effects on the Raman spectroscopic and electrical properties of GNRs were investigated experimentally for the first time. We demonstrated that the Raman G-band frequency of GNRs showed an approximate linear dependence on uniaxial strain with downshifts under strain at a rate of about -10 cm^{-1} per 1% strain (/%) for GNRs with a width of $\sim 20 \text{ nm}$. Uniaxial strain was found to tune the bandgap of GNRs significantly in a non-monotonic manner, with the bandgap varied between $\sim 25 \text{ meV}$ and $\sim 62 \text{ meV}$ under strain for a 19-nm-wide GNR. These results were in good agreement with theoretical modelings carried out. We have also leveraged the grant to explore the advanced electrical properties of graphene and carbon nanotubes for energy applications, in a paper published in *Nature Communications*. Our motivation is that hydrogen, as a clean energy resource, has been intensely investigated as an alternative to the diminishing fossil fuel. An effective way of producing high purity hydrogen is to electrochemically split water into hydrogen and oxygen in an electrolyzer but thus far there has been a lack of ideal water-reduction electrocatalyst for hydrogen evolution reaction (HER) catalyst except for precious metal platinum (Pt) and its alloys. In our work we found a nickel oxide/nickel (NiO/Ni) hetero-junction like structure attached to mildly oxidized carbon nanotube (NiO/Ni-CNT) exhibiting high HER catalytic activity close to commercial Pt/C catalysts in several types of basic solutions (pH=9.5-14).

Nanophotonics Enhanced Solar Cells

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Funding: \$184,425 (2014)

PROGRAM SCOPE

The over-arching objective of our project is to develop a fundamental understanding of optical physics of nanophotonic solar cells from a wave-optics perspective, and to use this understanding to develop pathways towards ultra-thin high-efficiency solar cells with thickness on the wavelength or deep sub-wavelength scales. In this project, the theoretical efforts will be directed to understand how nanophotonic engineering may impact both the open circuit voltage and the short-circuit current of ultra-thin solar cells, and towards the design of nanophotonic structures that may reach some of the theoretical limit. The theory efforts will be closely coupled with the experiments that explore a variety of ultra-thin absorber structures. The success of our project will open a pathway towards solar cell structures in a fundamentally different regime of performance as compared to conventional solar cells, with the potential to greatly enhance the efficiency/cost ratio of future solar cell architectures.

FY 2014 HIGHLIGHTS

In 2014 we have made the following advancements: 1. A comprehensive overview, published in Nature Materials, on how one can use dielectric nanostructures to improve the efficiency of solar cells. We argue that high-index dielectric systems, through its variety of optical resonance, provides numerous important opportunities for light trapping, anti-reflection, and open-circuit voltage enhancement that is crucial for solar cell performance enhancement. 2. A detailed balance analysis of single-nanowire solar cells, published in Nano Letters. We show that the Mie resonances of the single nanowire can be used to achieve absorption cross-section significant beyond the geometric cross-section of the wires and thus can be used to enhance the current of single nanowire cell. We also show that these resonances can be utilized for open-circuit voltage enhancement as well. And as a result one can accomplish significant efficiency enhancement in single nanowire cells by controlling optical modes. 3. A proposal to overcome the Shockley-Queisser limit, using only a single semiconductor, published in Nano Letters. For radiative solar cells, the open circuit voltage is no longer a property of the semiconductor, but rather depends critically on the optical modal structure of the cell. Therefore, through nanophotonic engineering, one can control the open circuit voltage of a cell. This opens the possibility of creating a multijunction cell from a single semiconductor, in which the open circuit voltage of each junction is controlled by the photonic environment of each junction. Using detailed balance analysis, we show that such a single-semiconductor multi-junction cell has the potential to overcome the Shockley-Queisser limit. 4. A theoretical elucidation of light trapping effects in photonic crystals, as published in Energy and Environmental Science. We show that the use of Van hove singularity in photonic crystal can be used to enhance light trapping efficiency.

Exploring the Impact of Local Environment on Charge Transfer States at Molecular Donor-Acceptor Heterojunctions

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Funding:	\$240,000 (2014-2017)

PROGRAM SCOPE

Charge transfer from a donor-type to an acceptor-type molecule forms the basis for the photovoltaic effect observed within conjugated molecular systems. The charge transfer (CT) state is a bound geminate charge pair that defines an intermediate state in both charge generation and recombination processes. As such, the CT state possesses a binding energy that still needs to be overcome in order to produce a free charge pair. While some important realizations have been made concerning CT states recently, there still remains a lack of fundamental knowledge regarding what controls CT state energy and the efficiency by which they may be dissociated, and whether or not Frenkel excitons become free charge via the formation of CT states. This research program sets out to comprehensively investigate the various nanoscale environmental factors that determine CT state behavior (dielectric, structural, dynamic, and energetic), as well as to quantify their spatial extent and density of states (DOS) energetic distribution. We will utilize sensitive spectral response measurements, impedance spectroscopy, X-ray scattering, and spectroscopic ellipsometry to probe the structure and optical response of thin films, as well as to extract dielectric properties. Surface-sensitive techniques such as ultraviolet photoelectron spectroscopy, inverse photoelectron spectroscopy, and X-ray photoelectron spectroscopy will be utilized to probe energy levels. Finally, time-resolved and steady-state photoluminescence, electroluminescence, electroabsorption, and pump-probe spectroscopy measurements will be used to probe CT state energetics and dynamics. In this way, the PIs assembled in this collaborative proposal represent a complementary team uniquely suited with the ability to transform our understanding of CT states.

FY 2014 HIGHLIGHTS

Thus far, we have begun to investigate the impact of disorder on CT states at a donor/acceptor (D/A) interface comprising rubrene and fullerene C_{60} . In one, micron-scale grains of rubrene template a relatively highly ordered fullerene layer, whereas the other consists of amorphous rubrene with more disordered C_{60} . The CT states at each of these heterojunctions are markedly distinct, the disordered one exhibiting a single CT feature below the optical edges of the constituent materials, whereas the ordered interface presents two features, the origin of which is currently being investigated via optical measurements such as spectral response and electroluminescence, as well as photoelectron spectroscopy. Additionally, we are making strides in identifying the width of the CT DOS distribution together with its occupation function under normal solar cell operating conditions by systematically exploring spectral shifts between CT photoluminescence and electroluminescence among various heterojunction materials and morphologies. These data, taken together with biased spectral response measurements, where the bias is either an applied voltage or background light, indicate that the occupation function depends strongly on DA interface morphology and is farther from equilibrium in bulk heterojunction devices than in their planar heterojunction counterparts.

Crystallization and Thermoelectric Transport in Semiconductor Micro- and Nanostructures Under Extreme Conditions

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Funding: \$150,000 (2014)

PROGRAM SCOPE

The objective of this project is to investigate non-equilibrium electro-thermal processes and the crystallization – amorphization behavior of materials. Self-heating of small structures leads to crystallization or melting under extreme thermal gradients and electric fields. The presence of strong electric fields breaks the generation-recombination equilibrium by moving the electrons and holes away from each other. This contribution to heat flow becomes the dominant mechanism with increased generation rates at higher temperatures. In the case of phase change materials nucleated sites perturb the generation-recombination process as well as the potential profile. Hence both carrier transport and electro-thermal processes dynamically change during operation. Experiments to investigate these phenomena are performed on lithographically defined nano-crystalline silicon microstructures and GeSbTe (225) nanostructures as well as thin films. Experimental setups are developed to perform high-temperature Seebeck and Hall measurements on thin film samples for materials characterization. The electro-thermal models are constructed using COMSOL multi-physics platform.

FY 2014 HIGHLIGHTS

We have developed our high-temperature Seebeck and Hall measurement setups and performed temperature dependent measurements on silicon and GeSbTe (225) thin films. We have observed a clear correlation between carrier activation energies and Seebeck coefficients for various polycrystalline fcc structures achieved by changing annealing temperature. The activation energies and the correlations we observe suggest that transport is limited by the grain boundaries. We have constructed numerical models that capture the nucleation and growth processes allowing us to model formation of nano-crystalline and poly-crystalline structures during annealing or self-heating. This dynamic materials model is integrated with electro-thermal models we have developed earlier. We are now finalizing a semiconductor model to accurately capture the electro-thermal processes due to non-equilibrium generation-recombination processes. This model assumes a drift-diffusion approximation in a non-isothermal system. We are hopeful that we can capture some of the interesting transport phenomena in non-homogenous and dynamic materials systems as the material goes through nucleation and growth or amorphization.

Atomic Clusters - Bare, Coated and Supported

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Funding: \$615,000 (2014-2017)

PROGRAM SCOPE

The objective of this project is to provide, by working closely with experimentalists, a fundamental understanding of the structure-property relationships of a novel class of highly electronegative clusters in the gas phase, study their interaction with support and counter-ions, and explore their potential as building blocks of materials with tailored properties. The project deals with four inter-related thematic areas of bare and supported clusters with rather uncommon properties. (1) Using first principles theory we design new highly electronegative clusters whose electron affinities far exceed that of chlorine and

validate their properties by working closely with experimentalists. These species, called super and hyperhalogens, usually consist of a metal atom at the core surrounded by halogen or oxygen atoms. Our goal is to create super and hyperhalogens without a metal, halogen, or oxygen atom by tailoring their size and composition and to push their electron affinities to values even higher than that currently known. (2) By suitably identifying counter ions we explore the ability of their corresponding salts to store hydrogen. (3) Superhalogens with magnetic moments are designed using transition metal atoms as key components. Their magnetic coupling is then studied by assembling them on graphene and noble metal substrates. (4) Using electronegative species as building blocks we explore the potential of multifunctional nanoparticles with Janus anisotropy for application in light harvesting. The computations are carried out using multiscale theoretical approach based on density functional theory (DFT) with hybrid and generalized gradient approximation based exchange-correlation functionals. When needed, quantum chemical methods such as Moller-Plesset perturbation theory and coupled cluster CCSD(T) are used to test the accuracy of the DFT based results.

FY 2014 HIGHLIGHTS

Publications: 30 publications in peer reviewed journals. Space does not permit to list all. Following is a reduced list: [1] Chen, H., Kong, X., Zheng, W., Yao, J., Kandalam, A. K., and Jena, P.: "Anomalous Property of $\text{Ag}(\text{BO}_2)_2$ Hyperhalogen: Does Spin-Orbit Coupling Matter?" *Chem. Phys. Chem.* 14, 3303(2013) [2] Knight, D. A., Zidan, R., Lascola, R., Mohtadi, R., Ling, C., Sivasubramaniam, P. K., Kaduk, J. A., Hwang, S.-J., Samanta, D., and Jena, P.: "Stabilization of Hydrogen Rich, Yet Highly Pyrophoric $\text{Al}(\text{BH}_4)_3$ via the Synthesis of the Hypersalt $\text{K}[\text{Al}(\text{BH}_4)_4]$ " *J. Phys. Chem. C* 117, 19905 (2013) [3] Kan, M., Zhou, J., Sun, Q., Kawazoe, Y., and Jena, P.: "Intrinsic Ferromagnetism in MnO_2 Monolayer" *J. Phys. Chem. Letters* 4, 3382 (2013) [4] Zhang, S., Wang, Q., Chen, X., and Jena, P.: "Stable Metallic 3D Metallic Phase of Carbon with Interlocking Hexagons", *Proc. Nat. Acad. Sci.* 110, 18809 (2013) [5] Zhang, S., Wang, Q., Kawazoe, Y., and Jena, P.: "Three Dimensional Metallic Boron Nitride", *J. Am. Chem. Soc.* 135, 18216 (2013) [6] Wang, H., Zhang, X., Jae Ko, Y., Grubisic, A., Li, X., Gantefoer, G., Schnoekel, H., Eichhorn, B. W., Lee, M. S., Jena, P., Kandalam, A., K., Kiran, B., and Bowen, K. H.: "Aluminum Zintl Anion Moieties within Sodium Aluminum Clusters" *J. Chem. Phys.* 140, 054301 (2014) [7] Tao, K., Sun, Q., Wang, Q., Stepanyuk, V., and Jena, P.: "Self-consistent Determination of Hubbard U for Explaining the Anomalous Magnetism of Gd_{13} Cluster", *Phys. Rev. B* 89, 085103 (2014) [8] Child, B., Gronett, S., and Jena, P.: "Aromatic Superhalogens", *Chemistry- A European Journal* 20, 4736 (2014) [9] Giri, S., Moore, C. H., Mcleskey, J. T., and Jena, P.: "Origin of Red-shift in the Photo absorption Peak in MEH-PPV Polymer", *J. Phys. Chem. C* 118, 13444 (2014) [10] Awnehss, A., Behera, S., El-Kaderi, H., and Jena, P.: "New insights into Carbon dioxide interactions with benzimidazole-linked polymers" *Chem. Comm.* 50, 3571 (2014). 11 Invited Talks at Conferences and academic institutes. One student awarded PhD.

Optical and Electrical Properties of III-Nitrides and Related Materials

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 Funding: \$158,000 (2014)

PROGRAM SCOPE

Hexagonal boron nitride (h-BN) is considered amongst the remaining frontiers in electronic and photonic materials. The scope of this research program is to extend our studies to the “newest” family member of the III-nitride material system, h-BN, and to address issues that have not yet been explored but are expected to profoundly influence our understanding on its fundamental properties and device applications. The proposed research efforts include: (1) Epi-growth. To further develop MOCVD growth processes for achieving high crystalline quality hexagonal phase BN epilayers with smooth surface morphology; (2) Deep UV (DUV) photoluminescence (PL) studies. DUV time-resolved PL will be employed to probe the optical properties and detailed band structures near the fundamental absorption edge and to extract information concerning the band structure, electron and hole effective masses, and exciton parameters in h-BN. The unique layered structure induced anisotropy in the optoelectronic properties in the out-of-plane and in-plane directions will be probed by various techniques, including polarization and time-resolved PL measurements; (3) Probing the roles of native defects and impurities. We will investigate the lateral and vertical transport properties and mechanisms of formation and elimination of native defects during MOCVD growth. The impact of native defects on the doping efficiency in h-BN will be probed. (4) Probing low-dimensional properties. Single layers or a few layers of h-BN will be deposited on sapphire substrate and AlN/sapphire template. The optical and electrical properties of 2D h-BN will be investigated and compared with 3D h-BN and graphene. Exciton binding energy, bandgap, and optical absorption of single sheet h-BN and their evolutions with the number of h-BN layers will be probed.

FY 2014 HIGHLIGHTS

Fundamentally important parameters and the origin of high optical efficiency in layered h-BN have been probed and device quality wafer-scale epitaxial layers have been realized. The measured exciton binding energy of 740 meV in h-BN represents the largest exciton binding energy ever reported for inorganic semiconductors. We have derived a generalized dispersion relation, which provides a direct relationship between the bandgap and effective mass for 2D semiconductors. The theoretical values are remarkably consistent with the exciton parameters deduced from the temperature dependence of the exciton lifetime. Our results revealed that the origin of the extremely high optical efficiency of h-BN is due to its large exciton binding energy and layered structure. The temperature dependence of the hole mobility in h-BN has been measured and is described by the form of T^{-a} with the exponent $a=3.02$, satisfying the 2D carrier transport limit dominated by the polar optical phonon scattering. The optical phonon energy deduced from the temperature dependence of the hole mobility is 192 meV (or 1546 /cm). The temperature dependence of the fundamental energy bandgap of h-BN sheets has been probed. The measured temperature coefficient of the bandgap of h-BN is about 0.43 meV/K, which is 6 times smaller than that of AlN. The weaker temperature dependence of the bandgap and emission wavelength of h-BN is a consequence of its layered structure. Our studies have demonstrated that h-BN represents an ideal platform to probe fundamental properties of 2D material systems and extend our understanding of the optical and charge carrier transport properties beyond the traditional III-nitride semiconductors. The unique properties of h-BN (weak temperature dependence of the bandgap and the extremely large exciton binding energy) can be utilized to fabricate photonic and electronic devices with exceptionally high thermal stability.

Bridging Atomistic and Continuum Scales in Phase-Field Modeling of Polycrystalline Pattern Evolution

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Funding: \$146,000 (2014)

PROGRAM SCOPE

The vast majority of structural and functional materials of energy relevance are polycrystalline. Those materials are fabricated and operate under a wide range of homologous temperature and stress levels. As a result, their performance, safety, and life time are strongly influenced by the response to stress of grain boundaries (GBs) and their complex interaction with crystalline defects and other materials interfaces. This renewal project is aimed at using state-of-the-art phase field methodologies to advance our fundamental understanding of the behavior of stressed polycrystalline structural and functional materials. It builds on our recent advances in phase field modeling to investigate the fundamental influence of stress in three important classes of energy related materials: (i) structural alloys, (ii) nanocrystalline materials, and (iii) Li-insertion electrode materials. For structural alloys, the proposed research focuses on understanding the effects of solute on grain coalescence through the combination of atomistic scale simulations and mesoscale phase field simulations that model *in situ* X-ray imaging studies of grain boundary (GB) dynamics during alloy solidification. Those experiments, carried out at DOE/BES facilities by our experimental collaborator Dr. Amy Clarke, provide a powerful new avenue to characterize solute effects on GB premelting in relation to hot tearing of structural alloys from the comparison of modeling and experiments. For nanocrystalline materials, we propose to use phase-field computation (PFC) simulations to explore basic mechanisms of stress-driven nanocrystalline grain growth on diffusive time scales, including the role of temperature and dopants. For Li-insertion electrode materials, we will develop a multiphysics phase field modeling platform to investigate complex failure mechanisms mediated by multiple cracks and their interaction with GBs during electrochemical cycling.

FY 2014 HIGHLIGHTS

We have shown both computationally and analytically that grain boundaries that exhibit shear-coupled motion become morphologically unstable in solid alloys that phase-separate into coherent domains of distinct chemical compositions. We have carried out simulations of continuum models demonstrating that this instability is mediated by long-range elastic interaction between compositional domains and grain boundaries. Simulations were carried out for parameters modeling phase-separation in Li-ion battery materials where Li intercalation in olivine particles leads to high dilatation volumes. In these materials, complex interactions between dislocations and Li-rich particles have been observed. The simulation methods employed include a nonlinear elastic model of dislocation dynamics and amplitude equations derived from the phase-field crystal approach. In addition, we have performed a linear stability analysis that predicts the range of unstable wavelengths in good quantitative agreement with simulations. In nonlinear stages, this pattern-forming instability leads to the breakup of low-angle grain boundaries, thereby strongly impacting microstructural evolution in a wide range of phase-separating materials.

Coupling Electrons, Phonons, and Photons for Nonequilibrium Transport Simulation

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Funding: \$171,497 (2014)

PROGRAM SCOPE

The objective of this project is to develop versatile computational tools for accurate simulation of the far-from-equilibrium and time-dependent quantum transport in realistic semiconductor nanostructures driven by high-intensity dc or ac electromagnetic fields. The key challenge in simulating nonequilibrium time-dependent transport is that one must capture the strong coupling between electrons, phonons, and electromagnetic fields in the same simulation, self-consistently and at every time step.

FY 2014 HIGHLIGHTS

With high-intensity fields, considerable energy is pumped into the electron system, which relaxes by transferring much of it to the lattice; thereby, both electronic and lattice (phonon) systems are far from equilibrium. We investigated the impact of nonequilibrium longitudinal optical (LO) phonons on electron transport in a midinfrared (mid-IR) GaAs-based quantum cascade laser over a range of temperatures (77–300 K) and fields using a newly developed coupled electron and phonon ensemble Monte Carlo (EMC) technique that explicitly takes into account the phonon momentum distribution. The overarching message is that nonequilibrium phonons are extremely important at low temperatures (for GaAs, below about 200 K) and negligible otherwise. At low temperatures and in the presence of nonequilibrium phonons, the electron-phonon absorption rate increases by one to two orders of magnitude, and this microscopic phenomenon has several manifestations. Nonequilibrium phonons lead to a selective enhancement of injection from the lowest injector state into the upper lasing level via LO phonon absorption, which results in higher modal gain and current at a given field and a threshold current density lower and considerably closer to experiment than the calculation with equilibrium phonons. By amplifying phonon absorption, nonequilibrium phonons impede electron energy relaxation and lead to broader electron distributions and higher electronic temperatures than the simulation with thermal phonons. [Y. B. Shi and I. Knezevic, 'Nonequilibrium phonon effects in midinfrared QCLs,' J. Appl. Phys. 116, 123105 (2014)].

EARLY CAREER: Evaluating the Oxidative, Photothermal and Electrical Stability of Colloidal Nanocrystal Solids

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PROGRAM SCOPE

IV-VI nanocrystal solids are a novel class of granular electronic materials with great technological potential (e.g., photodetectors, field-effect transistors, solar cells), but their oxidative and thermal instability present a barrier to practical applications. This project aims to determine the degradation mechanisms of IV-VI nanocrystal (NC) solids (primarily PbSe and PbS) and to introduce new chemical strategies to drastically improve their operating lifetimes and overall performance. The project will employ several *in situ* techniques to study oxidation and thermally-activated processes in NC solids. Variable temperature and variable ambient Scanning Kelvin Probe Microscopy will be developed to map the electronic structure of operating NC materials and monitor their electronic response to changing environmental conditions. *In situ* measurements of atomic and molecular diffusion within NC solids will be made using innovative photoelectron and infrared spectroscopy approaches. Variable-temperature X-ray diffraction studies will provide new insights into the thermal lability of NC solids, including the dynamics of low-temperature rotator phases. This suite of measurements will be used to determine if NC solids can be made sufficiently robust for real technological applications, such as large-scale photovoltaic power conversion. Three strategies to drastically improve the stability of NC materials will be pursued: (i) the use of robust molecular surface ligands, (ii) the conformal coating of NC films with thin inorganic shells grown by room-temperature atomic layer deposition, and (iii) *in situ* creation of core-shell NC solids by low-temperature solution-based ion exchange. Poor stability is a common feature of nanoscale electronic materials, yet stability is all too rarely the focus of basic research. Fundamental studies are therefore needed to elucidate the most important mechanisms of degradation and develop simple yet effective countermeasures.

FY 2014 HIGHLIGHTS

In this fiscal year of the project, we have used scanning Kelvin probe microscopy (SKPM) to map the electric potential across the cross section of operating PbS quantum dot (QD) solar cells as a function of applied bias and illumination. SKPM profiles show an absence of a significant space-charge region in the QD layer when paired with a variety of n-type window layers in a heterojunction configuration. Instead, we find that most of the applied potential is dropped in the n-type metal oxide layer, with very little in the QD layer. The lack of electric field in the QD film indicates the PbS layer is not fully depleted (contrary to what is commonly assumed in the field) and the photogenerated carriers likely reach the contact through diffusion rather than drift. Our results suggest the n-type window layer (ZnO or TiO₂) and the back contact (MoO_x/metal) serve as selective contacts for electron and hole extraction, respectively. This work directly impacts the design of future QD solar cell architectures for enhanced photogenerated charge extraction. We have also demonstrated the first Pb_x QD field-effect transistors (FETs) that do not suffer from the bias-stress effect at room temperature. The bias-stress effect is a phenomenon in which the drain current of a FET changes with time at constant bias conditions. Often such time-dependent currents are associated with charge trapping at the oxide surface resulting in time-dependent screening of the applied gate field. To eliminate the bias-stress effect, we used a pulse of H₂S gas to completely desorb volatile ligands coating the QDs, followed by infilling the QD film with amorphous alumina by low-temperature atomic layer deposition (ALD). We determined that elimination of the bias-stress effect depends on complete ligand removal, the formation of a clean, trap-free PbSe/PbS/alumina interface, and the sealing off of internal pore space to prevent proton migration in the gate field.

Light Trapping, Guiding and Concentrating for Maximizing Solar Energy Conversion

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Funding: \$400,000 (2014)

PROGRAM SCOPE

Photovoltaic devices convert light directly into electricity. It can offer a limitless, renewable source of energy provided that its light-capture and conversion-efficiency can be improved while using less semiconductor materials. Here, we propose a thin-film architecture to collect and absorb a broad spectrum of sunlight incident from all angles. Another benefit of using a thin film architecture is an improved carrier collection-efficiency. In this program, we will use a three-dimensional photonic crystal to trap and absorb sunlight in a thin slab of semiconductor and to achieve a much improved device performance. Under this program, fundamental innovations are proposed to explore a new optical effect, called “parallel-to-interface refraction”, to be realized in a 3D simple-cubic photonic crystal. This class of 3D photonic crystals, if properly designed, can refract sun-ray into a plane parallel to a photovoltaic cell’s surface over a broad wavelength and angle range. Our first long term scientific goal is to realize the parallel-to-interface refraction effect and experimentally demonstrate the predicted 75% solar absorption of all sunlight incident (400-1200nm) with one micrometer thick of silicon. We will also implement a multi-layer graded-index antireflection coating to minimize reflection and to improve the performance of our device. A new trend in solar collection and conversion is to bend light by 90-degrees using advanced photonics. Under this program, we propose to use a holographic thin film to diffract light by 90-degrees. Our second long term scientific goal is to realize a large-scale holographic film, capable of diffracting a wide spectrum of sunlight by 90-degrees. The three fundamental innovations are: (1) the use of volume hologram to achieve 90-degrees bending of sunlight from; (2) guiding and concentrating sunlight within the thin film by planar optics; (3) directing and converting sun light energy into a high efficiency photovoltaic cell.

FY 2014 HIGHLIGHTS

Over the past 12 months, our highlights are: (1) anomalous thermal radiation from a 3D active photonic-crystal; (2) efficient 90-degree light bending by volume hologram; (3) photonic architectures for high-Temperature Bose-Einstein Condensation. Non-Planckian thermal radiation from a 3D active photonic-crystal: We report the observation of unusual thermal radiation at elevated temperatures ($T=400-900K$) from a 3D metallic photonic-crystal (PhC) that includes a cavity. Upon thermal excitation, PhC’s emissive power at selective wavelengths does not correlate with its absorptivity - a deviation from Kirchhoff law. The ratio of PhC’s emissive power to that of a blackbody at nominally the same surface temperature also far exceeds one- a deviation from Planck’s law. It is further shown that, at resonance, photon gases are excited to beyond Bose-Einstein distribution. The intense EM-field near the metallic PhC/cavity interface may undergo strong feedback and even amplification of thermal radiation rate. Efficient 90-degree bending of light by volume hologram: we propose a new approach to realize a compact, lens-less and nearly all-angle solar-concentrator using a volume-holographic element. In our approach, top-incident light is diffracted by 90-degree into a volume hologram and, hence, converting solar collection problem into a guided-wave problem. We achieved 90-deg light-bending with high efficiency (70%) and without

the use of any external optics. Photonic architectures for high-Temperature Bose-Einstein Condensation (BEC): In this work, we demonstrate theoretically a route to simultaneously achieve very strong exciton-photon coupling and long polariton lifetime using a simple TiO₂ based photonic band gap (PBG) material sandwiching a planar quantum-well slab containing as few as three monolayers of the transition-metal dichalcogenide MoSe₂. This architecture provides a realistic, technologically accessible route toward equilibrium polariton BEC above room temperature.

Effect of Mechanical Strain and Quantum Electronic Stress on Physical Behavior of Bulk Materials and on Growth Property of Solid Nanomembranes

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Funding: \$294,000 (2014)

PROGRAM SCOPE

This project encompasses four diverse but correlated research thrusts: (1) to continue our traditional efforts in the area of strain induced self-assembly of nanostructures in heteroepitaxial growth of thin films, (2) to expand a new research direction in exploring the “quantum electronic stress” effect, a new conceptual extension over the conventional mechanical stress effect we developed recently, (3) to foster a new research direction in studying the effect of strain on topological and electronic phases, such as topological insulator, of thin films, and (4) theoretical studies of group-IV nanomembranes in close collaboration with experiments by Prof. Lagally funded by the “Materials Synthesis and Processing” program of the same DOE-BES division. The common theme of our research efforts will remain focusing on fundamental understanding of stress/strain effect on physical behaviors of materials and on growth property of thin films. The focused specific topics in the four thrusts include: (1) Nonlinear elastic effects on nucleation and growth of strained islands inside and outside a patterned pit, (2) Quantum electronic stress induced solid-state structural phase transitions, (3) Effect of strain on topological and electronic phase transitions in Bi(111) and Sb(111) thin films. (4) Effect of strain on growth, structural, mechanical and transport properties of Si and other solid nanomembranes. Our theoretical/computational project will employ a multi-scale approach, combining several state-of-the-art theoretical and computational techniques, ranging from density-functional-theory based first-principles electronic structure calculations to continuum elasticity theoretical modeling. Broadly, our project will have direct technological impact on advancing electronic and optoelectronic materials for energy applications, to fulfill the mission of the Department of Energy.

FY 2014 HIGHLIGHTS

(1) One recent highlight is our theoretical prediction of “Large-gap Quantum Spin Hall State on Si Substrate”. We show that Si(111) surface functionalized with 1/3 monolayer of halogen atoms exhibiting a trigonal superstructure, provides an ideal template for epitaxial growth of heavy metals like Bi which self-assemble into a hexagonal lattice with high kinetic and thermodynamic stability. Most remarkably, the Bi overlayer is ‘atomically’ bonded to but ‘electronically’ decoupled from the underlying Si substrate, exhibiting isolated quantum spin Hall (QSH) state with a large energy gap of 0.8 eV. This surprising phenomenon is originated from an intriguing substrate orbital filtering effect, which critically selects the

orbital composition around the Fermi level leading to different topological phases. The realization of topological edge states on semiconductor surfaces, which may be used as dissipationless interconnects, potentially will significantly advance the current semiconductor-based technology. (2) Another recent highlight is our discovery of a new form of a 2D material— sd^2 graphene. Graphene, made of sp^2 hybridized carbon, is characterized with a Dirac band, representative of its underlying 2D hexagonal lattice. Fundamental understanding of graphene has recently spurred a surge of searching for 2D topological quantum phases in solid-state materials. However, this new form of 2D material consists of sd^2 hybridized transition metal atoms in a hexagonal lattice, which we called sd^2 “graphene”. It is characterized with bond-centered electronic hopping, which transforms the apparent atomic hexagonal lattice into the physics of a kagome lattice that may exhibit a wide range of topological quantum phases. For example, room temperature quantum anomalous Hall states are demonstrated for one such lattice made of W. We expect these significant findings to open up a new avenue to explore novel materials based on conventional semiconductor technology.

Evolution of Atomic Structure and Bonding in Phase-Change a-GST and c-GST

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Funding: \$134,000 (2014)

PROGRAM SCOPE

Phase-change chalcogenide $Ge_2Sb_2Te_5$ (GST) is well suited for applications not only in rewritable data storage (optical CDs and DVDs), but also in phase-change non-volatile memory. This proposal builds upon our recent success and experience in uncovering the atomic-level structure and poly(morphism) in amorphous GST (a-GST). We will take advantage of our two-pronged computational/experimental approach, employing *ab initio* molecular-dynamics calculations and synchrotron X-ray and transmission electron microscopy experiments. Our goals are two-fold. 1) We aim to understand how the atomic structure and chemical bonding evolve in deeply supercooled GST, with emphasis on the temperature range from above the glass transition (and crystallization) temperature to room temperature. We will monitor the structural developments, especially the fraction of tetrahedrally coordinated Ge atoms and their stability (drift), the degree of Peierls-like distortion, and the fraction of homopolar bonds. 2) For the crystalline counterpart, the c-GST, we will determine the locations of Ge atoms, and assess the effects of defects/distortions on the degree of resonant bonding. In addition, we will characterize the defects induced by electrical current, to explore defect-triggered amorphization; this solid-state c to a collapse, in the absence of melting, has implications for electrically-switched memories.

FY 2014 HIGHLIGHTS

Using *ab initio* molecular dynamics simulations, we have monitored the evolution of atomic structure during the cooling of liquid $Ge_2Sb_2Te_5$ (GST). Irreducible rings (the shortest closed loops) are important in the theory of amorphous materials. We have revealed for the first time how four-membered (ABAB squares) and three-membered rings evolve with temperature in supercooled GST liquids. We found that the number of ABAB squares increases while that of three-membered rings decreases with decreasing temperature. In GST, Ge atoms are supposed to be bonded with Te atoms. However, this is not true in

real liquid GST. We have monitored the number of Ge-Ge bonds (“wrong bonds”) at different temperatures. We found an almost linear relationship between the number of wrong bonds and decreasing temperature. It indicates that the structural ordering in liquid GST evolves in the direction of decreasing homo-polar bonds with cooling, which may help to improve both topological and electronic ordering. Based on this trend, which would be expected to be more obvious if the cooling rate is lower in the simulation, or when the sample is aged for long times, the fraction of homopolar bonds may diminish, which may also lead to the reduction of the population of tetrahedrally bonded Ge. This atomic structural evolution may then help explain the “resistivity” increase (or drift) of the amorphous GST in data storage applications.

Frequency-Dependent Properties of Magnetic Nanoparticle Crystals

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Students: 1 Postdoctoral Fellow(s), 2 Graduate(s), 1 Undergraduate(s)
Funding: \$113,000 (2014)

PROGRAM SCOPE

This project builds on our magnetic nanoparticle synthesis and measurement capabilities, with a special interest in their frequency-dependent response. This project has supported the Ph.D. research of two graduate students (Krishna Chowdary, now faculty at Evergreen State College, Olympia, WA, and Ryan Booth, now a member of technical staff at the R. J. Lee Group, Pittsburgh, PA). Two of the 2014 papers acknowledging DOE support focused explicitly on the frequency-dependent behavior of magnetic nanoparticle assemblies: “Frequency-Dependent Magnetic Permeability of Fe₁₀Co₉₀ Nanocomposites”, K. M. Chowdary and S. A. Majetich, *J. Phys. D: Appl. Phys.* 47, 175001 (2014). “High-frequency permeability of Ni and Co particle assemblies”, V. K. Sakharov, R. A. Booth, and S. A. Majetich, *J. Appl. Phys.* 115, 17A517 (2014). The other two 2014 publications come from polarized neutron scattering on similar magnetic nanoparticle crystals: “Particle Moment Canting in CoFe₂O₄ Nanoparticles”, K. Hasz, Y. Ijiri, K. L. Krycka and J. A. Borchers, R. A. Booth, S. D. Oberdick, and S. A. Majetich, *Phys. Rev. B* 90, 180405(R) (2014). “Origin of Surface Canting within Fe₃O₄ Nanoparticles”, K. L. Krycka, J. A. Borchers, R. A. Booth, S. A. Majetich, Y. Ijiri, and J. J. Rhyne, *Phys. Rev. Lett.* 113, 147203 (2014). The Majetich portion of the neutron scattering work is solely supported by this DOE grant. We go to the NIST Center for Neutron Research for experiments and are active in data analysis, but the sample preparation is our unique contribution to the collaboration. Typically we travel to NIST twice a year, and students do neutron scattering in addition to their main projects. Part of the Ph.D. thesis research of Ryan Booth and Samuel Oberdick is based on neutron scattering work. Other parts of Sam Oberdick’s thesis research are supported by DARPA, and are clearly distinct from the fundamental studies supported by DOE.

FY 2014 HIGHLIGHTS

The main accomplishment this fiscal year was the improved understanding of the spin configuration within a magnetic nanoparticle, based on polarized neutron scattering. In simple models, monodomain nanoparticles have uniform magnetization throughout. However, many researchers have measured reduced magnetization in nanoparticles, relative to the bulk material, which has previously explained the reduction in terms of a surface spin glass, magnetic dead layer, or more complex ordered

arrangements. Our small angle neutron scattering experiments on magnetic nanoparticle crystals ruled out most of these models. Applying a magnetic field to monodisperse Fe_3O_4 nanoparticle crystals causes their surface spins to cant uniformly, while the spins in the core align parallel to the field. The effect is reversible and temperature-dependent. Because the origin of this symmetry breaking was unclear, we developed our own model that included exchange, anisotropy, magnetostatic, and Zeeman energies. Because the exchange energy depends on the number of magnetic neighbors, the orientation of the surface spins is most sensitive to the other energies. We found that the Zeeman energy exceeded the anisotropy and magnetostatic contributions for Fe_3O_4 nanoparticles, and that the competition between exchange and Zeeman effects led to surface spin canting. To test the model further, we prepared two other types of magnetic nanoparticle crystals and did polarized neutron scattering measurements on them. In CoFe_2O_4 nanoparticles, the anisotropy energy is ten times higher than for Fe_3O_4 , and no shell formation was seen, as predicted by the model. MnFe_2O_4 nanoparticles were also investigated, because they have comparable magnetization to that of Fe_3O_4 but a much lower Curie temperature, and therefore weaker exchange. Preliminary results show a strong field-dependence to the scattering, and the data are currently being analyzed.

Rational Design of Hybrid Nanocrystal/Silicone Architectures: From Fundamentals of Energy Transfer to Applications of Energy Sustainability

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Funding: \$233,000 (2014)

PROGRAM SCOPE

The proposed program is aimed to provide a fundamental understanding and explore practical utility of novel thin-film photovoltaic (PV) structures based on energy transfer (ET) between highly absorbing colloidal nanocrystal quantum dots (NQDs) and highly conducting Si semiconductor components combined in hybrid nanostructures. The light's energy is initially absorbed by NQDs and then transferred, via radiative (RET) and non-radiative (NRET) energy transfer, into a thin flexible Si layer for further electron-hole separation and transport. The strength and novelty of our approach is based on the fact that NRET and RET are longer distance interactions as compared to standard charge transfer and do not involve physical transfer of charge carriers across an interface, thus largely avoiding associated interface quality issues. We aim to determine the experimental conditions for efficient directional ET from optically thick NQD multilayers into underlying nanostructured Si substrates optimized for electron-hole pair separation and electrical transport. Our experimental efforts are supplemented by extensive theoretical modeling of NRET and RET conditions as to achieve optimum efficiencies. We are developing a new class of NQDs with enhanced photophysical properties (superior photostability and long-lived multiexcitonic states) in the near-infrared spectral region necessary for efficient sunlight harvesting. Furthermore, we have been utilizing ET-based platform as a testbed to study advanced concepts for Si sensitization. These include plasmonic and molecular antennae effects to extend ET interaction range, collection of sub-bandgap photons and study of various methods to avoid thermalization losses when harvesting high-energy photons. The last effort aims to explore conditions

for multiexciton ET from novel NQDs and initial experiments in singlet exciton fission in phosphorescent (other than NQDs) materials coupled to Si substrates.

FY 2014 HIGHLIGHTS

In the first year we concentrated on the development of the grafting strategies and approaches to create densely packed, multilayer size-gradient nanocrystal structures with directed energy flow towards the silicon substrate. We proceeded with layer-by-layer deposition using amine-modified linkers to prepare nanocrystal multilayers. We applied time-resolved optical spectroscopy methods to measure energy transfer (ET) efficiency through the nanocrystal bi-layers and into Si and have shown that our linking strategy is effective in creating defect-free nanocrystal solids. We have also started to explore an alternative/complementary assembly technique, where dense nanocrystal arrays are obtained via slow sedimentation from the films on the water surface. Our first results have shown considerable promise as we obtained very uniform and nearly closely-packed NQD monolayers on Si. In collaboration with colleagues at LANL we pursued the development of novel, photostable infrared-active nanocrystals able to augment absorption and ET in the infrared portion of the solar spectrum. New class of lead-based, core/shell PbSe/CdSe and PbS/CdS nanocrystals has been developed that show enhanced optical absorption and emission properties in the infrared ($\sim 1 \mu\text{m}$) spectral region. In parallel, we performed studies of the multiexciton emission properties of similar (emitting in the visible) CdSe/CdS ultraphotostable nanocrystals. ET from multiexcitons is supposed to further enhance solar conversion efficiencies and our focus on studying of the biexciton emission efficiencies in different types of nanocrystals allows us to explore the applicability of this approach in hybrid systems. Based on our successes with nanocrystal grafting, we started to develop electrically addressable Si samples and recorded steady-state photocurrent enhancement in nanocrystal-sensitized hybrid structures.

Surface Engineering by Simultaneous Action of Multiple External Fields

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Funding: \$220,000 (2014)

PROGRAM SCOPE

This research program aims at enabling surface engineering strategies based on the fundamental understanding and predictive modeling of the surface morphological response of solid materials subjected to the combined action of multiple external forces. We focus on the surface morphological evolution and stability of electrically conducting and semiconducting solids under the simultaneous application of mechanical stresses, electric fields, and temperature gradients; materials of interest include fcc metals, such as Cu, Ag, and Al, and semiconductors, such as Si and chemically functionalized or defect engineered graphene-based metamaterials. We emphasize: identifying the conditions under which the multiply driven surface morphology is stable, exploring the complexity of the corresponding various morphologically stable surface patterns, and stabilizing and controlling nanoscale patterns on surfaces. Specifically, we investigate the morphological response to the combined action of multiple external forces of bulk solid surfaces, surfaces of thin films grown epitaxially on thick or thin substrates, as well as nanoscale surface features such as coherently strained epitaxial islands on substrate surfaces.

The analysis of complex pattern formation as a result of the driven evolution of surface features (directed assembly), including distributions of single-layer epitaxial islands and vacancy islands, offers new paradigms of multiply driven surface nanopatterning. The research is based on a modeling approach that combines theoretical analyses of surface/feature morphological stability with self-consistent dynamical simulations of driven surface/feature evolution based on properly parameterized continuum and multi-scale surface transport models that we develop. Employing these models, we conduct systematic studies of the effects of multiple forcing conditions, varied over a broad range of material and operating parameters, on surface morphological response.

FY 2014 HIGHLIGHTS

We examined the surface morphological stability of conducting crystalline elastic solids in uniaxial tension under the action of a temperature gradient alone and simultaneously with an electric field. We established that properly directed and stronger-than-critical thermal gradients and electric fields can be used both individually and synergistically to stabilize the planar surface morphology. Our findings set the stage for an effective, practical approach to inhibiting morphological instabilities that cause surface cracking of crystalline solids. We have developed a weakly nonlinear theory for the occurrence of tip-splitting instabilities that cause formation of secondary ripples on surfaces of stressed solids, without or with the simultaneous action of externally applied electric fields and/or thermal gradients, and the number of ripples that form on the surface as a function of surface perturbation wavelength. We have conducted a systematic simulation study of an approach to surface nanopatterning through electric-field-driven assembly of single-layer epitaxial islands on face-centered cubic crystalline substrates. We have discovered entire classes of complex pattern formation starting from either a large single island or an assembly of relatively small islands that undergo a sequence of coalescence and break-up events. We have determined the dependence of the nanopattern features on the single island size or the assembly's intrinsic geometrical parameters, island edge diffusional anisotropy parameters, and the duration of application of the electric field. We have also studied the assembly of crystals of colloidal particles and established: the effects of the attractive inter-particle potential range on the phase behavior and polymorphic transitions between different crystalline configurations, how the assembly can be controlled to result in close-packed crystalline structures, and the equilibrium colloidal crystal shape as a function of the crystal size.

Acceptor Defects in ZnO and Related Materials

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PROGRAM SCOPE

Zinc oxide (ZnO) is an electronic material with desirable properties for a range of energy applications. ZnO is a wide band gap (3.4 eV) semiconductor that emits light in the near-UV region of the spectrum, with high efficiency. Despite its advantages, the lack of fundamental knowledge about dopants and defects presents an obstacle to the development of practical devices. Reliable p-type doping, required for high-performance transistors, lasers, or light-emitting diodes, has been elusive. The scientific

literature contains numerous reports that nitrogen doping can produce p-type ZnO. However, recent first-principles calculations, and experimental results from the prior DOE funding period, suggest that nitrogen is a deep acceptor, with the acceptor level 1.3 eV above the valence-band maximum. The current project will provide a fundamental understanding of defects in ZnO that could lead to reliable p-type conductivity. First, alloying ZnO with the chalcogens sulfur, selenium, or tellurium will raise the valence band. By tuning the valence band, one may realize a reduced nitrogen acceptor binding energy. This approach can be summarized as “if you cannot bring the acceptor to the valence band, bring the valence band to the acceptor.” Alkali dopants (lithium and sodium), which have lower binding energies than nitrogen, could prove especially fruitful. A second strategy for p-type doping is suggested by studies on ZnO nanocrystals, which show evidence for an acceptor level 0.46 eV above the valence-band maximum. The identity of this acceptor is currently unknown. In this project, the fundamental properties of acceptor defects in ZnO and related materials will be investigated. The results of these optical and electrical characterization studies could provide the basis for the long-sought goal of reliable p-type doping of ZnO. More broadly, this investigation will provide physical insight into defects in oxide semiconductors, in bulk crystals, thin films, and nanocrystals.

FY 2014 HIGHLIGHTS

(1) Acceptors in ZnO nanocrystals: Using commercial ZnO nanocrystals of diameter ~ 90 nm, we provide experimental evidence that they contain hydrogenic acceptors. Infrared (IR) absorption peaks and a photoluminescence (PL) peak were observed, consistent with those previously observed in ~ 20 nm diameter ZnO nanocrystals. High field (W-band) electron paramagnetic resonance (EPR) measurements revealed an axial center with $g_{(\text{perp})} = 2.0015$ and $g_{//} = 2.0056$, along with an isotropic center at $g = 2.0035$. The two defect centers detected by EPR are not necessarily the same as the acceptor observed by IR and PL. (2) Annealing of ZnO thin films: The objective of this study is to find annealing conditions that enhance UV photoluminescence (PL) at ~ 3.3 eV and understand the underlying defect dynamics. Annealing experiments were performed on two as-grown ZnO thin films: one film was annealed in O_2 and the other in an Ar environment. The annealing temperature and times were 900°C and 1 hour, respectively. ZnO films were grown by sputtering for 1 hour at 250°C on quartz substrates. The as-grown sample exhibits a very weak UV-PL, and a strong visible PL at ~ 2.8 eV, tentatively attributed to zinc interstitials. Annealing under an O_2 environment diminished the 2.8 eV band; however, new defect centers were created that activate the PL at 2.18 eV, attributed to oxygen interstitials. The UV PL shows a significant increase. These results can be explained in terms of the low migration barrier for Zn interstitials that enable them to diffuse either to the lattice sites or out to the environment. However, the oxygen rich environment saturates the sample, resulting in oxygen interstitial defect centers. Annealing in an Ar environment resulted in reduction of the 2.8 eV band.

Interfaces in Electronic and Structural Materials

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Funding: \$387,000 (2014-2017)

PROGRAM SCOPE

Development of revolutionary new materials for future energy applications relies on progress in fundamental understanding of materials' interfaces and our ability to predict, design and control their properties. The objective of this program is to advance the fundamental understanding of interfaces, especially in materials subject to deformations and high temperatures, and to develop new methods for computational prediction of interface properties. The proposed research focuses on interfaces in thermoelectric materials using bismuth telluride Bi_2Te_3 as a model system. Specific goals include investigations of: (1) effect of crystallographic characteristics, applied stresses, temperatures and chemical composition on atomic structure, thermodynamic characteristics, mechanical strength and motion of internal interfaces in Bi_2Te_3 alloys, and (2) effect of interfaces on thermal conductivity of this material. The main approach to achieving these goals is based on atomistic computer simulation methods, primarily molecular dynamics and a variety of Monte Carlo techniques. These methods are capable of delivering critical atomic-level information about the interface structures and predicting mechanical, thermodynamic and kinetic properties of interfaces. Extensive first principles calculations will be performed for calibration of a new many-body angular-dependent interatomic potential that will be developed for Bi_2Te_3 alloys in order to enable quantitative large-scale atomistic simulations. The results of the simulations will be validated against experimental data for grain boundary structures, mechanical and thermoelectric properties of Bi_2Te_3 . The project is expected to make a significant impact on the state of knowledge in interface science by improving fundamental understanding of mechanical, thermal and dynamical properties of interfaces, especially in thermoelectric materials. This goal is relevant to the BES mission and is aligned with DOE's Grand Challenges.

FY 2014 HIGHLIGHTS

1. Phase transformations at interfaces present a profound fundamental interest as complex examples of phase transitions in low-dimensional systems. We have developed a new methodology of atomistic simulations that has revealed multiple grain boundary phases and reversible first-order phase transformations between them. Furthermore, we have demonstrated that interface phase transformations can strongly impact transport properties, for example atomic diffusion along grain boundaries. Atomistic calculations of Ag diffusion in two different structural phases of a Cu grain boundary demonstrate excellent agreement with experimental measurements, providing the first convincing evidence for the existence of structural phase transformations in high-angle grain boundaries and demonstrate the possibility of their detection by boundary diffusion measurements and atomistic simulations. The interface phase transformations can also influence electric and thermal resistance of interfaces and offer a means of achieving new properties via design optimal microstructures. 2. Massive first-principle DFT calculations have been conducted for various crystalline structures of Bi and Te. The obtained first-principles database has been used to construct many-body angular-dependent interatomic potentials for Bi and Te. The potentials accurately reproduce a wide range of properties of these elements, including structural energies, phase transformations, melting temperatures, phonon dispersion relations, thermal expansion, point defect formation and migration energies and many other properties. Work is currently underway to develop a similar first-principles database for developing the Bi-Te cross-interaction functions describing the Bi-Te binary system, particularly the bismuth telluride Bi_2Te_3 .

Colloidal Semiconductor Dense Films for Red, Green, and Blue Lasers

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Funding: \$420,000 (2014-2017)

PROGRAM SCOPE

The primary objective of this project is to create a solid thin film photonic material platform which can leverage recent work to advance colloidal semiconductors towards practical single material based lasers across the visible spectrum. We seek to understand multiple physical properties of very dense, closely packed CdSe-based II-VI semiconductor core-shell solid thin films which, contrary to earlier work in the field, have now been shown to retain the high luminescence efficiencies (up to 90% and beyond) which the red, green, and blue (RGB) quantum dots exhibit in the starting high concentration solution form. Inherently, we take advantage of the ability to define any specific wavelength of emission within RGB color range by control of the quantum dot (QD) size.

FY 2014 HIGHLIGHTS

Colloidal quantum dots (CQD) are now making their entry to full-color displays, endowed by their brightness and single-material base. By contrast, many obstacles have been encountered in their use towards lasers. We have now demonstrated optically pumped distributed feedback (DFB) lasers, based on close-packed, solid films self-assembled from type-I CQDs. Notably, the single mode CQD-DFB lasers could reach such a low threshold as to be pumpable with a compact pulsed source in a quasi-continuous wave regime. Our results show the spatially and temporally coherent laser beam outputs with power of 400 microwatts and an internal quantum efficiency of 32%. Further, we have extended the surface emitting distributed feedback (DFB) lasers from the red across green and blue from densely packed colloidal quantum dot (CQD) films by varying the quantum dot size. The solid CQD films were deposited on periodic grating patterns to enable 2nd-order DFB lasing action at mere 120, 280, and 330 microjoules per square centimeter of optical pumping energy densities for red, green, and blue DFB lasers, respectively. The lasers operated in single mode operation with less than 1 nanometer of full-width-half-maximum. We measured far-field patterns showing high degree of spatial beam coherence. Specifically, by taking advantage of single exciton optical gain regime from our engineered CQDs, we can significantly suppress the Auger recombination to reduce lasing threshold and achieve quasi-steady state, optically pumped operation.

Metamaterials as a Platform for the Development of Novel Materials for Energy Applications

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Funding: \$99,999 (2014)

PROGRAM SCOPE

The PI will explore the fundamental properties of metamaterials (MMs) and their potential for energy applications in support of the mission of the Department of Energy and the office of Basic Energy Sciences. The advent of metamaterials provides novel electromagnetic responses and enables study of exotic materials – particularly in the microwave through THz and up into far IR parts of the electromagnetic (EM) spectrum – providing an ideal platform to explore a rich variety of science, from optics, condensed matter physics, materials science, to nanoscience. The PI proposes to advance the understanding of these materials through fundamental investigations of the experimental and theoretical properties of metamaterials and to provide a knowledge base for the discovery, prediction and design of new materials with novel structures, functions, and properties. The research activities emphasize the computational design and fabrication of the materials, and the characterization of their electromagnetic properties. There are a number of novel properties of the proposed materials which make them ideally suited for basic research with a view toward potential energy applications:

- Absorptivities and emissivities of metamaterials may be tailored, enabling applications such as thermophotovoltaics and lighting. Other materials lack this engineerability thus adding complexity to a given design.
- Approaches based on metamaterials may be readily scaled to various energy ranges, i.e. THz, infrared, optical. Metamaterials do not depend on, and are not limited by, the inherent electronic band structures of the constituent materials.
- Alternative metamaterial designs can be utilized for similar electromagnetic response, enabling flexibility.
- Metamaterials are multifunctional, i.e. tailored absorptivities and emissivities naturally incorporate filtering and optimization, reducing the necessity of additional materials.

FY 2014 HIGHLIGHTS

(1) Dynamic 3 State Metamaterial A 3-state tunable metasurface that shows all wave-matter interaction states (Reflection, Transmission, and Absorption) in one device was demonstrated. Our initial work was performed at X-band (8 to 14 GHz). Working at microwave frequencies simplified the fabrication process allowing us focus on the fundamental science behind creating a switchable 3-state system. The tuning was achieved by reverse biasing varactor diodes mounted onto the metasurface. By changing the capacitance of the varactor diodes, the impedance of the metasurface at one unique frequency is altered and thus the absorption, reflection and transmission spectra of the metasurface are tuned. S-parameter extraction is used to show the shifting of resonance peaks, and the extracted impedance results explain the 3-state tuning phenomena. Investigation into materials suitable for high temperature near infrared (NIR) Metamaterials Metamaterial emitters for thermal photovoltaic (TPV) applications can be expected to be used at temperatures on the order of 1000K. At these temperatures however most of the properties and characteristics of traditionally used materials are not ideal. The temperatures will exceed the melting point for most metals and certain combinations of materials will form eutectic mixtures (i.e. silicon and gold). We have begun work on examining different materials for use in metamaterial absorbers/emitters. For conventional metamaterial designs we are looking at high melting point metals such as platinum and dielectrics such as aluminum oxide to prevent eutectic formation.

Exploring the Impact of the Local Environment on Charge Transfer States at Molecular Donor-Acceptor Heterojunctions

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Principal Investigator: Barry Rand

Sr. Investigator(s): Antoine Kahn; Princeton University
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Funding: \$580,002 (2014-2017)

PROGRAM SCOPE

Charge transfer from a donor-type to an acceptor-type molecule forms the basis for the photovoltaic effect observed within conjugated molecular systems. The charge transfer (CT) state is a bound geminate charge pair that defines an intermediate state in both charge generation and recombination processes. As such, the CT state possesses a binding energy that still needs to be overcome in order to produce a free charge pair. While some important realizations have been made concerning CT states recently, there still remains a lack of fundamental knowledge regarding what controls CT state energy and the efficiency by which they may be dissociated, and whether or not Frenkel excitons become free charge via the formation of CT states. This research program sets out to comprehensively investigate the various nanoscale environmental factors that determine CT state behavior (dielectric, structural, dynamic, and energetic), as well as to quantify their spatial extent and density of states (DOS) energetic distribution. We will utilize sensitive spectral response measurements, impedance spectroscopy, X-ray scattering, and spectroscopic ellipsometry to probe the structure and optical response of thin films, as well as to extract dielectric properties. Surface-sensitive techniques such as ultraviolet photoelectron spectroscopy, inverse photoelectron spectroscopy, and X-ray photoelectron spectroscopy will be utilized to probe energy levels. Finally, time-resolved and steady-state photoluminescence, electroluminescence, electroabsorption, and pump-probe spectroscopy measurements will be used to probe CT state energetics and dynamics. In this way, the PIs assembled in this collaborative proposal represent a complementary team uniquely suited with the ability to transform our understanding of CT states.

FY 2014 HIGHLIGHTS

Thus far, we have begun to investigate the impact of disorder on CT states at a donor/acceptor (DA) interface comprising rubrene and fullerene C₆₀. In one, micron-scale grains of rubrene template a relatively highly ordered fullerene layer, whereas the other consists of amorphous rubrene with more disordered C₆₀. The CT states at each of these heterojunctions are markedly distinct, the disordered one exhibiting a single CT feature below the optical edges of the constituent materials, whereas the ordered interface presents two features, the origin of which is currently being investigated via optical measurements such as spectral response and electroluminescence, as well as photoelectron spectroscopy. Additionally, we are making strides in identifying the width of the CT DOS distribution together with its occupation function under normal solar cell operating conditions by systematically exploring spectral shifts between CT photoluminescence and electroluminescence among various heterojunction materials and morphologies. These data, taken together with biased spectral response measurements, where the bias is either an applied voltage or background light, indicate that the occupation function depends strongly on DA interface morphology and is farther from equilibrium in bulk heterojunction devices than in their planar heterojunction counterparts.

Collaborative Research: Polymeric Multiferroics

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Sr. Investigator(s):

Students: 1 Postdoctoral Fellow(s), 1 Graduate(s), 1 Undergraduate(s)

Funding: \$47,000 (2014)

The University of Maryland part of this project is listed separately under Principal Investigator: Manfred Wuttig

PROGRAM SCOPE

The goal of this project is to investigate room temperature magnetism, spin resonance, magnetoelectric coupling of polymeric multiferroics. A unique organic multiferroic material system with the understanding of magnetism, magneto-transport, magnetic field effects and magnetoelectric coupling, could have potential impacts on organic sensor, memories, and potentially high T_c organic superconductors. A new family of organic charge-transfer complexes has been emerged as a fascinating opportunity for the development of all-organic ferroelectrics and spintronics due to its weak hyperfine interaction and low spin-orbit coupling; nevertheless, direct observations of room temperature magnetic spin ordering have yet to be accomplished in organic charge-transfer complexes. Furthermore, room temperature magnetoelectric coupling effect hitherto known multiferroics, is anticipated in organic donor-acceptor complexes because of magnetic field effects on charge-transfer dipoles, yet this is also unexplored. The PI seeks to fundamental understanding of the synthetic control of organic complexes to demonstrate and explore room temperature multiferroicity. Our experimental work is a joint effort with Dr. Manfred Wuttig at the University of Maryland, College Park.

FY 2014 HIGHLIGHTS

We have synthesized thiophene nanowire/Au nanocluster nanohybrids as a prototypical charge-transfer system, which exhibits magnetic field effects and spin-optoelectronic properties (*Angewandte Chemie International Edition*, 53, 7316, 2014). The experimental results have been confirmed through theoretical modeling. By applying external stimuli on organic multiferroics, some key findings are observed as following: 1) spin correlated transport behavior of crystalline polymeric multiferroics due to thermal induced triplet bipolarons; 2) electric field and light controlled magnetic susceptibility and magneto-dielectric coupling through the control of singlet and triplet charge transfer states; 3) Magnetic field effects and photon-controlled ferroelectricity in polymeric multiferroics at room temperature (*ACS Nano*, 8, 3671, 2014; *Advanced Materials*, DOI:10.1002/adma.201403396, 2014, selected as the Frontispiece for *Advanced Materials*; *Nano Letters*, 14, 5308, 2014; *Scientific Report*, DOI:10.1038/srep06126, 2014).

High Performance Bulk Thermoelectric Materials

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Sr. Investigator(s):

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Funding: \$233,747 (2013-2014)

PROGRAM SCOPE

Solid-state thermoelectric energy conversion is a promising technology to convert the waste heat into electricity or to cool devices/systems in an environmentally friendly manner, leading to significant energy saving and reduced environmental impact. We proposed to study ways to enhance thermoelectric properties in a number of materials by a nanocomposite approach using a quick and economic ball milling and hot pressing process. The work involves improving of the thermoelectric figure of merit (ZT) of a few existing good thermoelectric materials. This project will also provide educational opportunities to graduate students, postdocs, and visiting professors on clean energy research.

FY 2014 HIGHLIGHTS

In fiscal year 2014, we published eight papers, one in Nature Nanotechnology, one in Nature Communication, two in Nano Energy, one in PRB, one in APL, one in Light: Science & Applications, and one in New Journal of Physics. One student has graduated with a PhD degree. In these eight papers, we have a few important developments: 1. We found CoO nanoparticles made by ball milling are efficient catalyst for water splitting under one Sun radiation. 2. We discovered a new way to make metallic nanomesh exhibiting outstanding flexibility, light transmittance, and electrical conductivity. These new materials will be used as flexible transparent electrodes for flexible electronics. 3. We drastically improved the figure-of-merit of MgAgSb. With such improvement, it is aimed for wide spread usage for heat to electricity conversion in temperatures lower than 300°C.

Defect Studies of CZTSe & Related Thin Film Photovoltaic Materials

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Funding: \$300,000 (2014)

PROGRAM SCOPE

Thin film photovoltaics have seen great advances in the past 3 years with three materials (CdTe, Cu(In,Ga)Se₂, and CH₃NH₃PbI₃) achieving high efficiency solar cells at 19% or greater. Cu₂ZnSn(S,Se)₄ or CZTSSe is very close in crystalline and electronic structure to Cu(In,Ga)Se₂ which, if fundamental understanding and control of its electronic defects can be achieved, could be used for building terawatts of photovoltaic energy generation unconstrained by supplies of its constituent elements because they are earth abundant. This project seeks fundamental understanding of the electronic states present in CZTSSe and their origins in the bulk or in grain boundaries. This is being pursued through capacitive spectroscopy measurements such as deep level transient spectroscopy primarily. We are also studying the composition fluctuations on the mesoscale of 30 nm to 30 um using transmission x-ray tomography and attempting to link this to observed electronic defects. Lastly, we are investigating bulk CZTS samples including both single crystals and those containing grain and phase boundaries in order to understand how these structural defects manifest electronically.

FY 2014 HIGHLIGHTS

In 2014 we continued our study of the minority electron trapping defect which we located recently in CZTS samples fabricated from nanoparticle precursors at Purdue. We established that it exists as a distribution of energy separations from the conduction band centered on 0.59 eV and that its electron capture cross-section is $2 \times 10^{14} \text{ cm}^2$. Combining simulation with experiment, we established reliable values for its total concentration at $10^{15} / \text{cm}^3$ and showed how it (somewhat counterintuitively) can fill and empty with electrons during the experiment. Also the simulation allowed projection of the effects of this defect on the minority carrier lifetime and open circuit voltage of CZTS photovoltaic devices. This accounting for the 'missing' V_{oc} in CZTS indicates that another mechanism is probably also operating - a finding that has been speculative to date.

Study of Materials and Interface Properties for High-Efficiency Spin Injection: Spin Dependent Quantum Phenomena in Ferromagnetic Graph

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Funding: \$130,000 (2014)

PROGRAM SCOPE

A focus of this BES-funded project is to develop a better understanding of magnetic/non-magnetic interfaces for more efficient spin injection. Spin injection can be accomplished by a spin-polarized charge current or a pure spin current without any charge current. Interfaces play a critical role in both. During the funding period, we propose to study the interfaces of magnetic oxide/organic semiconductors, magnetic metal (oxide)/graphene, magnetic oxide/metals, magnetic oxide/topological insulators, etc. We grow and characterize magnetic oxide thin films such as LaSrMnO, yttrium iron garnet first, and then fabricate heterostructures using various techniques. We employ magneto-transport, spin pumping, and thermal/thermoelectric transport to investigate the properties of relevant interfaces and their effects on spin injection and spin transport.

FY 2014 HIGHLIGHTS

One highlight of the funded project is the finding of the physical origin of the magneto-resistance in heterostructures of heavy metals with yttrium iron garnet (YIG) which is a ferri-magnetic insulator. Controversies existed about the newly discovered magnetoresistance effects in such a system. One mechanism is called the spin Hall magnetoresistance which is due to the transport of spin currents across the interface of metal/magnetic insulator. By performing a systematic temperature dependence study, we have found the characteristic features predicted for this spin current induced magnetoresistance. In addition, we studied the interplay between the spin Hall magnetoresistance and the conventional anisotropic magnetoresistance as the spin diffusion length is varied (PRL). Another highlight is the study of the proximity-induced ferromagnetism in graphene using YIG as a substrate. In a Scientific Reports article, we demonstrated the proximity effect in graphene/STO. We adopted the same transfer technique to fabricate graphene/YIG and found ferromagnetism in graphene. If graphene is spin-polarized by the proximity effect, a variety of interesting phenomena can be realized. Similar

interface effect has been investigated in metal/metal bilayer systems such as Pd/NiFe and Ta/NiFe. We have identified various contributions such as the proximity-induced anomalous Nernst effect and spin Seebeck effect in the systems. In FY 2014, we have published four papers, including one in Phys. Rev. Lett., one in Scientific Reports, one in New Journal of Physics, and one in Appl. Phys. Lett. The PI gave an invited talk at the APS March meeting. We submitted a paper to Phys. Rev. Lett. in May, 2014 which was accepted in December (appeared in Jan. 2015).

EARLY CAREER: Nanostructured Colloidal Self-Assembly and Controlled Alignment of Anisotropic Nanoparticles

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Funding: \$150,000 (2014)

PROGRAM SCOPE

Harvesting, storage, and conversion of energy among its different forms strongly depend on available materials and their properties. Self-assembly of nano-sized functional units is an exceptionally promising way of designing inexpensive artificial composite materials with new macroscopic physical behavior and properties. The main objective of this project is to explore self-organization of anisotropic nanoparticles into colloidal composites with tunable ordered structures. The research is focusing on understanding and control of self-assembly of metal and semiconductor nanoparticles, as well as on material behavior arising from their ordered self-organization and alignment. Fundamental studies of shape-dependent colloidal interactions and ordering of quantum dots and plasmonic metal nanoparticles are expected to reveal underpinning physical mechanisms that guide mesoscale morphology and ultimately determine material properties of the self-assembled composites. These properties are characterized and correlated with hierarchical structures and composition. Analytical and numerical modeling of colloidal interactions and material properties provide important insights at different stages of this project. This research may enable new, cheaper, and more efficient renewable energy technologies, a new breed of energy-efficient information displays and consumer devices, as well as a fertile ground for new basic science.

FY 2014 HIGHLIGHTS

According to the original plan of the proposal, we have focused on synthesis, dispersion, and switching of various plasmonic metal nanoparticles in thermotropic liquid crystals. We have developed plasmonic nematic colloids with facile switching of ordered anisotropic metal nanoparticle ensembles by low-voltage fields and low-intensity light. Practical guest-host devices, in which dichroic dye molecules follow electrical switching of a liquid crystal host, remain elusive for decades despite promising efficient displays and emergent applications such as smart windows. This is mainly because of poor stability, surface precipitation, and limited means for property engineering of the dyes. To overcome these challenges, we develop plasmonic metal nanoparticle analogs of dichroic guest-host liquid crystals. Nematic dispersions of aligned anisotropic gold nanoparticles are obtained by polymer passivation of their surfaces to impose weak tangential boundary conditions for orientation of anisotropic host molecules. Control of the ensuing surface interactions leads to long-range ordered colloidal dispersions, allowing for collective optical and electrical switching of rod- and platelet-like nanoparticles. Our

research resulted in the following publications: [1] Q. Liu, Y. Yuan, and I. I. Smalyukh. Electrically and Optically Tunable Plasmonic Guest-Host Liquid Crystals. *Nano Lett.* 14, 4071–4077 (2014). [2.] Q. Liu, M. Campbell, J. S. Evans, I. I. Smalyukh. “Orientationally Ordered Colloidal Co-Dispersions of Gold Nanorods and Cellulose Nanocrystals.” *Advanced Materials* 26, 7178–7184 (2014). [3] Q. Liu, J. Tang, Y. Zhang, A. Martinez, S. Wang, S. He, T. White, and I. I. Smalyukh. Shape-dependent dispersion and alignment of non-aggregating plasmonic gold nanoparticles in lyotropic and thermotropic liquid crystals. *Phys Rev E* 89, 052505 (2014). [4] M. Campbell, Q. Liu, A. Sanders, J. Evans, I.I. Smalyukh. Preparation of Nanocomposite Plasmonic Films...*Materials* 7, 3021-3033 (2014).

Ground State Magnetism and Cooperative Phenomena in Correlated Electron Oxide Materials

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Funding: \$140,000 (2014)

PROGRAM SCOPE

Transition-metal oxides exhibit rich complexity in their fundamental physical properties determined by the intricate interplay between structural, electronic and magnetic degrees of freedom. This project would focus on correlated systems like Ruddlesden-Popper type double layer perovskites where anisotropy is likely to play an even more crucial role than in pseudocubic perovskites. Special attention would be given to exploring the role of dimensionality through systematic experimental studies and establishing correlation between the structure, electronic and magnetic properties in single crystals, thin films and nanoparticles. In continued studies on the $\text{Pr}_{1-x}\text{Sr}_x\text{CoO}_3$ cobaltite system we intend to explore the effect of reduced dimensionality (thin films and nanoparticles) on the intriguing coupled structural/magnetocrystalline anisotropy driven transition observed in polycrystalline systems in our prior work. In addition we would also extensively probe the fundamental ground state physics in the $\text{Ca}_3\text{Co}_2\text{O}_6$ system which has spin chains arranged on a triangular lattice geometry. This results in competing magnetic ground states that can be tuned by temperature, field and structural changes. All these systems are of current interest and have important unresolved issues that we intend to solve through our combination of DC, AC and RF magnetization studies coupled with neutron scattering. In addition to our signature RF susceptibility and magneto-caloric effect (MCE) experiments, we would initiate broadband high frequency magnetoimpedance measurements to probe spin dynamics and spin Seebeck effect (SSE) measurements to investigate the coupling between spin and heat transport in these complex oxides.

FY 2014 HIGHLIGHTS

Our major accomplishments during the 2013-2014 period include: (1) Using magneto-caloric effect (MCE) method to establish a new magnetic phase diagram for the spin chain cobaltite $\text{Ca}_3\text{Co}_2\text{O}_6$ that exhibits geometric frustration with intrinsic low-dimensionality; (2) Discovery of an inverse magnetocaloric effect (IMCE) in hydrothermally synthesized single crystalline $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ nanowires; (3) First systematic investigation into the collective contributions of interface and surface spins to the exchange bias (EB) in $\text{Fe}/\gamma\text{-Fe}_2\text{O}_3$ core-shell nanoparticle systems; (4) Exploring a new approach of tuning EB in hybrid $\text{Au-Fe}_3\text{O}_4$ nanostructures using an interfacial strain. In particular, we have established a

comprehensive phase diagram of $\text{Ca}_3\text{Co}_2\text{O}_6$ from the temperature and magnetic field dependence of magnetic entropy change. Our new findings assert the recent theoretical predictions of the existence of a spin-density wave ground state at zero field, providing new insights into the collective magnetic phenomena in geometrically frustrated 1D magnets (Physical Review B 89, 144414, 2014). We have discovered the IMCE in $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ nanowires, which is absent in its bulk counterpart. Our study points to the importance of disordered surface spins and sheds light on the origin of the EB effect in nanostructured manganites (Nanotechnology 24, 505712, 2013). We have demonstrated, in $\text{Fe}/\gamma\text{-Fe}_2\text{O}_3$ core-shell nanoparticles, that there exists a critical particle size (~ 10 nm), above which the spins at the interface between Fe and $\gamma\text{-Fe}_2\text{O}_3$ contribute primarily to the EB, but below which the surface spin effect is dominant. Such knowledge is key to manipulating EB in magnetic nanostructures for spintronics applications (Applied Physics Letters 104, 072407, 2014). We have demonstrated an interfacial strain between Au and Fe_3O_4 as a driving force for enhanced surface spin disordering and hence the EB effect in the Au- Fe_3O_4 composite nanoparticle system.

EARLY CAREER: Probing Coherent States of Light and Matter in Two-Dimensional Semiconductors

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Funding: \$750,000 (2014-2018)

PROGRAM SCOPE

The objective of this program is to investigate cavity-enhanced optical coupling between photonic resonators and two-dimensional monolayer semiconductors such as transition metal dichalcogenides. When reduced to a single atomic layer, the band structure of these nanomaterials displays degenerate valleys in momentum space that can be separately addressed by polarized light. We propose to explore a fundamentally new regime of interfacing photons with nano-materials using excitations of specific valley quantum number, potentially revealing new avenues for probing coherent phenomena in layered 2D systems. Drawing on progress in photonics, nanoscale materials, and quantum optics, our approach combines monolayer material synthesis with solid-state quantum optics and on-chip photonic device circuits to realize a new vision of valley-sensitive quantum manipulation using light. This project will explore several main directions. We study mechanisms of valley-specific light-matter coupling in monolayer semiconductors. Enabling this, we seek to advance strategies for integrating these materials into dielectric photonic resonators with exquisite control over the material's optical environment. In the proposed experiments, we will investigate new methods of probing coherent phenomena in 2D materials using hybrid light-matter excitations. The ability to engineer light-matter interactions with the next-generation of layered nano-materials will have long-term impact by advancing possibilities for controlling matter using light, such as coherent preparation and control of valley states and exploiting symmetries of low-dimensional semiconductor materials in integrated photonic and polaritonic devices.

FY 2014 HIGHLIGHTS

So far, we have achieved optical evidence for exciton-polaritons in large-area monolayers of transition metal dichalcogenides (TMDCs) integrated with dielectric Bragg reflector mirrors. We have observed optical coupling using white-light reflectivity, revealing a measured light-matter coupling constant the

same order-of-magnitude as predicted by associated calculations We have now started applying these methods to observe light-matter coupling in related layered materials grown by our collaborators. Further, we have demonstrated the coupling of MoS₂ monolayers to photonic resonators through measurement of cavity-coupled photoluminescence collected by a high-magnification objective. For our next steps, we will pursue technical advances to translate the measurements to low temperatures where valley polarization becomes important and to illuminate the mechanisms for energy transfer between monolayer materials and photonic devices. This initial progress will lead to more detailed understanding of the coupling strength and excitation dynamics in this hybrid light-matter system.

Spin Functionality Through Complex Oxide Heteroepitaxy

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Funding: \$250,000 (2014)

PROGRAM SCOPE

In this program, we address a strategic materials challenge associated with spin electronics that may be an energy efficient alternative to charge based electronics where power dissipation during dynamic operation and standby places limits on scaling. We focus on the development of novel complex oxide thin films and heterostructures with spin functionality where surfaces/interfaces and coherent epitaxial strain play a critical role in the realization of the long-range magnetic order. Many of these emergent magnetic phenomena are not accessible in bulk form and depend on the atomically precise synthesis of the materials. Therefore the development of atomically precise complex oxide thin films and heterostructures with spin functionality generated at surfaces/interfaces or by epitaxial strain is key to the success of this program. In particular, we have studied (i) heterostructures in which the interfaces gives rise to spin functionality not observed in the two constituent materials and engineered by carrier mediated exchange interactions or valence discontinuities at ferromagnetic interfaces and (ii) thin films in which epitaxial strain can induce spin-state transitions or metal-insulator transitions to stabilize ferromagnetic and/or metallic ground states. Our approach combines atomic scale epitaxy with careful local structural, electronic and magnetic characterization in the form of x-ray absorption spectroscopy, x-ray magnetic circular dichroism, x-ray resonant magnetic scattering, magnetic force microscopy, transmission electron microscopy and electron energy loss spectroscopy as well as macroscopic magnetic and electronic characterization.

FY 2014 HIGHLIGHTS

We have demonstrated interfacial ferromagnetism in CaMnO₃ based superlattices, ferromagnetism in epitaxial cobaltite thin films, as well as unexpected behavior in ultrathin films of CaMnO₃. One of our major accomplishments has been to demonstrate that interfacial ferromagnetism is generated in just one single unit cell of CaMnO₃ as predicted by theory. Through a combination of polarized neutron reflectometry and exchange bias measurements, we definitively showed that the interfacial ferromagnetism can only be explained in terms of a ferromagnetic double exchange interaction among the Mn ions in a single unit cell of the CaMnO₃ layers at each interface. Recent results indicated that the exchange bias continues to increase and showed no sign of saturation at CaMnO₃ thicknesses of up to

20 unit cells. This trend can be explained in terms of a long range antiferromagnetic correlation observed in neutron diffraction experiments. We also demonstrated that this emergent interfacial ferromagnetism observed in $\text{CaRuO}_3/\text{CaMnO}_3$ superlattices is a much more general phenomena. We found similar emergent behavior when we replace the itinerant metal CaRuO_3 with LaNiO_3 . Since LaNiO_3 undergoes a thickness dependent metal-insulator transition, we have been able to demonstrate that the metallicity in the layer adjacent to the CaMnO_3 is an essential ingredient to the interfacial ferromagnetism. We have also definitively demonstrated the origin of ferromagnetism in epitaxial LaCoO_3 thin films not found in the bulk. The presence of high spin (HS) Co^{3+} and Co^{2+} , in addition to low spin (LS) Co^{3+} , in different proportions depending on the substrate choice suggests that a combination of superexchange interactions based on correlated hopping among HS and LS Co^{3+} and superexchange interactions among HS Co^{2+} and LS Co^{3+} in the presence of ordered oxygen vacancies is responsible for the observed ferromagnetic ground states.

Understanding Structure-Property Relationships in Ferroelectric Oxides

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Funding: \$95,000 (2014)

PROGRAM SCOPE

We are focusing on the small ion perovskite E-phase systems and extending structural studies down to temperatures below 10 K, where the total measured polarization rapidly increases and where contact with DFT ($T=0$) measurements may be made. Moving towards materials with possible device applications, we will examine nano-scale materials as a path toward high density storage. Detailed measurement of the structural properties and dynamics will be conducted over a range of length scales from atomic to mesoscopic scale using, x-ray absorption spectroscopy, x-ray diffuse scattering, x-ray and neutron pair distribution analysis and high resolution x-ray diffraction. Changes in vibration modes which occur with the onset of polarization will be probed with temperature and pressure dependent infrared absorption spectroscopy. The multiple length scale synchrotron based measurements may assist in developing more detailed models of these materials and possibly lead to device applications. An important contribution of this work will be the training of graduate students and postdoctoral researchers in materials synthesis, synchrotron based spectroscopy and x-ray scattering techniques.

FY 2014 HIGHLIGHTS

[1] "Detailed Structural Studies Polar State in Freestanding Strontium Titanate Nanoparticles" T. A. Tyson *et al*, Appl. Phys. Lett. 105, 091901 (2014). Monodispersed strontium titanate nanoparticles were prepared and studied in detail. It is found that ~ 10 nm as-prepared stoichiometric nanoparticles are in a polar structural state (with possibly ferroelectric properties) over a broad temperature range. A tetragonal structure is found as the particle size is reduced. The results indicate that nanoscale motifs of SrTiO_3 may be utilized in data storage as assembled nano-particle arrays in applications where chemical stability, temperature stability and low toxicity are critical issues. [2] "Absence of significant structural changes near the magnetic ordering temperature in small-ion rare earth perovskite RMnO_3 " T. Yu *et al*, J. Phys.: Condens. Matter 26, 495402 (2014). Detailed structural measurements on multiple length

scales were conducted on a new perovskite, ScMnO_3 , and on orthorhombic LuMnO_3 as a benchmark. The measurements place upper limits on any structural changes to be at most one order of magnitude lower than density functional theory predictions. [3] "Structural changes related to the magnetic transitions in hexagonal InMnO_3 " T. Yu *et al*, Phys. Rev. B. 90, 174106 (2014). Two magnetic ordering transitions are found in InMnO_3 . Multiple length scale structural measurements reveal enhanced local distortion found to be connected with tilting of the MnO_5 polyhedra as temperature is reduced. Coupling is observed between the lattice and the spin manifested as changes in the structure near both of the magnetic ordering temperatures (at ~ 42 K and ~ 118 K). External parameters such as pressure are expected to modify the coupling. [4] "Pressure Dependent Structural Changes and Predicted Electrical Polarization in Perovskite RMnO_3 " T. Wu *et al*, submitted to Phys. Rev. B. (see arXiv link arxiv.org/pdf/1403.7998).

Uncovering and Surmounting Loss Mechanisms in Nitride Light Emitters

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Funding: \$120,000 (2014)

PROGRAM SCOPE

The overarching aim of the present project is to understand energy losses in nitride light emitting diodes (LEDs) and devise methods of overcoming them. Light emission from solid-state light emitters is still suffering from limited efficiency. This constitutes a key issue for the nitride light-emitting diodes (LEDs) that form the basis for solid-state lighting, but LEDs based on conventional semiconductors also exhibit limited efficiencies. Understanding the microscopic origin of various physical pathways that lead to those losses is crucial for the improvement of future devices. We study loss mechanisms based on cutting-edge first-principles calculations as well as semi-empirical modeling. The aim is to calculate radiative and nonradiative recombination rates without any fitting to experiment. Shockley-Read-Hall recombination will be quantified for impurities and point defects relevant to the quantum-well structures. Absorption due to free and bound carriers will be evaluated. Limitations in hole transport, which are severely impeding carrier distribution over multiple wells, will also be addressed. The calculation of nonradiative recombination rates requires methodological developments that will be valuable and applicable to other materials system as well. Our goal is for our insights to result in recommendations for improved materials growth, as well as in novel structures, based on band-structure, wave-function, and electric-field engineering, aimed at promoting carrier distribution and alleviating the effects of any remaining nonradiative recombination or absorption processes.

FY 2014 HIGHLIGHTS

(1) Nonradiative carrier capture rates: One of the goals is to understand the microscopic origin of Shockley-Read-Hall (SRH) recombination centers in nitride light emitters. SRH is proportional to the first power of the carrier density, and has a distinct impact on overall device efficiency. Recombination consists of two capture events: electron capture and hole capture. We have developed a practical first-principles methodology to calculate carrier capture coefficients. All the ingredients for the theory, including vibrational frequencies and electron-phonon coupling constants, are determined consistently

from hybrid functional calculations. We have also put forward a methodology to deal with bulk scattering states during a nonradiative capture process. The methodology has been applied to selected defects in GaN and ZnO, chosen as benchmark cases because of the availability of reliable experimental results. The agreement with experiment is excellent. (2) First-principles luminescence lineshapes: The study of radiative transitions provides a lot of useful information about defect geometries, vibrational properties, etc. It also serves as a further benchmark for the accuracy and reliability of our methodologies for treating electron-phonon interactions. Building on our development of a methodology to calculate luminescence lineshapes for defects with very strong electron-phonon coupling, we have now developed an approach for studying defects with moderate coupling, a case in which luminescence lineshapes have more structure, and often many contributing phonon frequencies can be identified. As a test case, the methodology was applied to the nitrogen-vacancy (NV) center in diamond, a defect which serves as an excellent benchmark. Very good agreement was obtained.

Mesoscale Interfacial Dynamics in Magnetolectric Nanocomposites

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Funding: \$106,770 (2014)

PROGRAM SCOPE

Multiferroic materials have a coexistence of at least two ferroic orders (ferroelectric, ferromagnetic, or ferroelastic). In multiferroic materials, the coupling interaction between the different order parameters can produce new phenomena, such as the magnetoelectric (ME) effect. The ME response is the appearance of an electric polarization P upon applying a magnetic field H , and/or the appearance of a magnetization M upon applying an electric field E . Magnetoelectricity has been observed as an intrinsic effect in some natural materials at low temperature; however, such single phase materials suffer from extremely weak ME exchange. Better alternatives are two-phase composites consisting of magnetostrictive and piezoelectric phases, which have been shown to have large ME coefficients. Said composites exploit a unique product ME tensor property that depends upon the individual strictions of the piezoelectric and magnetostrictive phases, the elastic stiffness and integrity of the interphase interfaces, the phase distribution and the dimensionality of its connectivity, and any elastic constraint; amongst other things. The specific objectives of this program are as following (i) development of new self-assembled morphologies and anisotropies in two phase ME epitaxial layers; (ii) determine microstructure of the interfaces between magnetic and piezoelectric phases, using electron microscopies; and (iii) find the correlation between local and bulk magnetoelectric responses to develop physical relationships that elucidate the fundamental nature of linear and non-linear coupling at varying length scales.

FY 2014 HIGHLIGHTS

In the last year, we have made progress in the following areas. (i) We have shown the volatile and nonvolatile changes in the M-H curves with electric field in Mn doped CoFe_2O_4 layers grown on $(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - x [PbTiO_3] (PMN-PT) crystals. These studies have demonstrated a large electric field tunable magnetic anisotropy, in particular an electric field induced magnetic phase transformation was

observed for layers grown on (110) oriented substrates. The phase transformation can be reversible or irreversible, resulting in volatile and/or nonvolatile magnetic easy axis rotations respectively. (ii) Growth and characterization of magnetostrictive Fe-Ga layers deposited on PMN-PT crystals. It was shown that an electric field can irreversibly and reversibly modulate the magnetization. (iii) Integration of perovskite/multiferroic layers on semiconducting substrates to provide understanding of transport mechanisms and reveal the control parameters for nonlinear responses. We have performed high resolution transmission electron microscopy to investigate the interface of the high-k materials deposited on various orientation (100), (110) and (111) of Ge layer using molecular beam epitaxy (MBE) on GaAs substrate. Valence and conduction band offset of dielectrics on crystallographically oriented Ge layers, and the band alignments of the integrated BaTiO₃- BiFeO₃ (BTO-BFO) solid solution layers were quantified. (iv) Characterization of interfacial interactions in PZT/CFO/PZT magnetoelectric trilayers grown on Pt/Ti/Si substrates.

Thermodynamic, Kinetic and Electrochemical Studies on Mixed Proton, Oxygen Ion and Electron (Hole) Conductors

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Funding: \$158,000 (2014)

PROGRAM SCOPE

The principal objective of the work is to conduct thermodynamic, kinetic and electrochemical studies on mixed proton, oxygen ion and electron (hole) conductors. The work involves theory and experiments. Transport processes are analyzed using linear non-equilibrium thermodynamics. Onsager coefficients including cross terms in coupled transport are determined. Transport processes in fuel cells, electrolyzers and lithium ion batteries are examined using linear non-equilibrium thermodynamics. Role of low level electronic transport on chemical potentials of electrically neutral species is assessed. Relative directions of ionic and electronic flows determine whether or not chemical potentials are bounded within the electrolyte. It is shown that if the ionic (e.g. H⁺, O²⁻, Li⁺) and electronic currents are parallel, the chemical potentials of the corresponding neutral species (H₂, O₂, Li) in the electrolyte can exceed electrode values. This can lead to either electrolyte reduction or precipitation (and pressurization) of neutral species (H₂, O₂, Li) and failure of the electrochemical devices. Thermodynamic stability of electrochemical devices such as fuel cells, electrolyzers, lithium ion batteries is examined. Experimental part involves the use of AC and DC techniques to investigate transport properties (ionic and electronic conductivities, Onsager transport coefficients) and a study of local thermodynamics by embedded probes. Using these techniques, spatial distributions of chemical potentials of electrically neutral species (H₂, O₂, Li) inside an electrolyte are measured. The role of coupled transport is also examined in the stability of proton exchange membrane fuel cell cathodes. The thermodynamics of catalyst-support interaction are examined both theoretically and experimentally. This includes a study of electrochemical Ostwald ripening of platinum-based nanocatalysts and the role of catalyst support.

FY 2014 HIGHLIGHTS

(1) Developed a novel technique for the measurement of electronic conductivity of predominantly ionic conductors by an embedded electrode method. The technique measures exceptionally low values of electronic conductivity with no redistribution of composition. Electronic conductivity of yttria-stabilized zirconia (YSZ) was measured at as low a temperature as 500°C. A paper is published in J. Electrochem. Soc. (2015). (2) Examined electrochemically induced pressure due to coupled transport of ionic and electronic pressure, which demonstrates the role of unbounded chemical potentials. A paper was published in Procedia IUTAM (2014). (3) Theoretical analysis is conducted on reversible fuel cells based on mixed ionic electronic conducting electrolyte materials. It is shown that some level of electronic conductivity through the electrolyte is beneficial since it tends to smooth out the chemical potential variation through the electrolyte membrane. A manuscript has been submitted to the Int. J. of Hydrogen Energy (2014). (4) A parametric equation was developed which describes voltage vs. current density polarization curves of solid oxide fuel cells in terms of out-of-cell fundamental measurements of the kinetics of electrocatalysis and gas diffusion through porous media. Using the model, for the first time realistic characteristics of fuel cells can be predicted in terms of fundamental materials property measurements. A manuscript based on this work will be submitted for publication within the next month. (5) Theoretically examined the role of catalyst size distribution and catalyst-support interactions on platinum catalyst stability. Mono-dispersed catalysts resist Ostwald ripening due to very low thermodynamic driving force for growth and thus exhibit excellent stability. It was also shown that contact angle between the catalyst and the support governs stability. An invited talk was presented at the Fall Meeting of the Electrochemical Society. A manuscript is under preparation.

Nanocrystal-Based Dyads for Solar to Electric Energy Conversion

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Funding: \$185,000 (2014)

The Duke University part of this project is listed separately under Principal Investigator: David Beratan

PROGRAM SCOPE

We are exploring nanoparticle-based materials that promise to provide a systematic and modular approach to creating a new generation of solar energy conversion devices. The project team (comprised of researchers at U. Pittsburgh, Duke Univ., and the Weizmann Institute of Science) is working to develop a systematic and quantitative approach to creating supramolecular assemblies of linked nanoparticles that function as charge transfer elements.

FY 2014 HIGHLIGHTS

(1) Ligand Tuning of Valence Band Offsets: We have studied, both experimentally and computationally, the electronic energies of CdSe nanoparticles (NPs) as a function of size and capping ligand. These results show how the energy position and the size-dependent behavior of the energy bands of CdSe can be modulated by the chemical nature of the capping ligand. -- J. Phys. Chem. C. (2013) 22401–22411. (2) Electric-field Effect on the Charge Transfer between Semiconductor Nanoparticles and Conjugated

Polymers: Excitonic solar cells, such as organic bulk heterojunction devices, utilize donor-acceptor (D-A) energy offsets to dissociate electron-hole pairs, whereas conventional p-n junction solar cells employ an internal electric field for the same purpose. Recently, we created electrostatic assemblies of conjugated polymers and semiconductor nanoparticles that incorporate static electric fields which promote electron transfer. -- Phys. Chem. Chem. Phys. 16 (2014), 5066 – 5070. (3) Depleted Bulk-Heterojunction: We investigated the effects of annealing on the detailed interface structure and energy conversion behavior of TiO₂/PbS heterojunction solar cells. We showed that annealing causes intermixing of the TiO₂ and PbS phases, thereby increasing the junction area within the depleted bulk heterojunction (DBH) layer and promoting the carrier extraction from PbS QDs to TiO₂. -- J. Phys. Chem. C 118 (2014) 14749-14758. (4) Plasmonic Effects on Solar to Electrical Conversion: We examined how the placement of core-shell plasmonic particles influenced the conversion efficiency in PbS/ TiO₂ bulk heterojunction cells. This work shows that the solar to electrical conversion efficiency is improved by two effects: 1) the enhanced scattering and electric fields caused by the plasmonic particles and 2) the enhanced light scattering caused by morphological changes in the back electrode which result from the plasmonic particle incorporation. -- Solar Energy Materials and Solar Cells 128 (2014).

Fundamental Piezotronic and Piezo-Phototronic Effects in Nanowires

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Principal Investigator: Zhong Wang
Sr. Investigator(s):
Students: 1 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding: \$137,123 (2014)

PROGRAM SCOPE

The fundamental effect of mechanically-induced polarization charges on electronic and optoelectronic processes of charge carriers in piezoelectric materials has been long overlooked, due to the fact that conventional piezoelectric materials are mostly insulating. Semiconductor materials such as ZnO, GaN and CdS are also piezoelectric but not as extensively utilized in piezoelectricity due to their relatively small piezoelectric coefficients. The coupling between strain-induced polarization and charge carrier process in piezoelectric semiconductors, known as piezotronic/piezo-phototronic effect and first proposed by the PI in 2006 and 2009, respectively, provides fundamental approaches to modulate electronics/optoelectronics characteristics by tuning the junction/contact properties, which is unavailable in existing methods without modifying the interface structure or chemistry. Piezoelectric polarization charges can serve as a “gate” controlling signal that effectively controls the carrier transport across the interface/junction. This is the piezotronic effect. These polarization charges can also effectively modulate the optoelectronic processes, such as generation, separation, diffusion and/or recombination, of charge carriers. This is the piezo-phototronic effect. A fundamental study is essential for advancing early theoretical/experimental work and exploring the nature of these two emerging effects. The objective of this proposal is to extend the scope of piezotronics and piezo-phototronics and develop a more comprehensive understanding of these emerging effects in different material/structure systems for potential applications. Then, the fundamental theory will be explored to study the charge processes in piezotronic structures. This proposal is a renewal of prior funded BES DOE (DE-FG02-07ER46394) project.

FY 2014 HIGHLIGHTS

The PI's group has made major accomplishments for this project within FY 2014, focusing on the fundamental study of piezoelectric polarization charges on carriers' electronic and optoelectronic processes in low-dimensional piezoelectric semiconductor. Specifically, the PI's group has

- Reported the first experimental investigation of piezoelectricity and piezotronic effect in single atomic layer 2D MoS₂ and its application in mechanical energy harvesting and piezotronic sensing (Nature, 514, 470-474, 2014).
- Demonstrated the first piezotronic effect enhanced Schottky-contact ZnO micro/nanowire humidity sensor (Nano Res. 7, 1083-1091, 2014).
- Developed the first ZnO Nanowire Film Based Temperature Sensor with enhanced sensing by piezotronic effect (ACS Applied Materials & Interfaces, 6, 5955-5961, 2014).
- Carried out detailed study on piezo-phototronic effect in optoelectronic devices based on wurtzite semiconductor nanowires (Physical Chemistry Chemical Physics, 16, 2790-2800, 2014).
- Reviewed the progress and provided prospective for the field of piezotronics and piezo-phototronics by two invited review papers in high-profile journals (Nano Today, 8, 619-642, 2013, and National Science Review, 1, 62-90, 2014).

EARLY CAREER: Plasmon-Mediated Electrochemical Reactions: the Influence of Nanoparticle Structure

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Funding: \$150,000 (2014)

PROGRAM SCOPE

This project seeks to identify whether coupling electrochemical reactions to plasmonic nanoparticle electrodes can impact the redox potentials of the reaction, thereby lowering energy barriers to effect desired reactions of interest. To study electrochemical reactions on the nanoscale, we use optical readouts of the redox state of molecules, including surface-enhanced Raman scattering and fluorescence.

FY 2014 HIGHLIGHTS

We have characterized the intensity-dependent redox response of our optical probe, Nile Blue, showing that light alone can impact redox potentials, although not as dramatically as when the probe is coupled to nanoparticle electrodes. We have also shown that coupling the Nile Blue to nanoparticle aggregates changes the electrochemical behavior of the probe, although the mechanism for the observed behavior is still under investigation. We have developed a simple, inexpensive strategy for fabricating nanoparticle electrodes using block copolymer lithography and have created arrays of electrodes that span the relevant wavelength window of the Nile Blue absorption and emission. So far, the redox potentials track with the spectrum of the probe, rather than the plasmon resonance of the electrode substrate. Nonetheless, they can be favorably shifted, based on preliminary data.

Charge Transfer Across the Boundary of Photon-Harvesting Nanocrystals

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Funding: \$157,000 (2014)

PROGRAM SCOPE

The goal of this project is to understand the fundamental processes that govern interfacial charge transfer across nanocrystal boundaries. We carry out use-inspired fundamental studies of charge transport in nanocrystal assemblies, and from nanocrystals into other semiconductor materials with two principal goals: (1) to understand and control electronic structure and transport properties across nanoscale interfaces, and (2) to create confined-but-connected nanostructures that balance quantum-confinement and –coupling for optimized light capture and charge transport. Major themes include the role of dimensionality in charge and energy transport and the physical and chemical properties of nanocrystal surfaces. The work is done in the context of photovoltaic devices, but the knowledge that we gain will also be relevant to a variety of settings, including molecular electronics, sensors, light emitters, and electrocatalysis. The device configurations that we consider combine silicon and solution-synthesized nanocrystals in inexpensive, efficient solid-state solar cells.

FY 2014 HIGHLIGHTS

Atomically-coherent nanocrystal assemblies offer the potential for size-engineered electronic and optical properties, along with band-like carrier transport. We have demonstrated assembly and epitaxial connection of PbSe nanocrystals into paracrystalline superlattices. Self-assembly at a liquid-liquid interface is employed along with in-situ small-angle x-ray scattering. Superlattice order with a correlation distance more than 100 nm is revealed by x-ray scattering and transmission electron microscopy. Assemblies with square and hexagonal symmetries have been produced. Measurements of field-effect transistor structures indicate that charge-carrier transport in these films is thermally-activated, with a delocalization length of ~ 10 nm. These results are consistent with calculations, which underscore the critical role of energy and structural disorders on the properties of the assembly. Nanosheets (or colloidal quantum wells) represent the limiting case of atomically-coherent structures, and are of major interest in their own right. To date there are only a couple reports of synthesis of lead-salt nanosheets. By increasing the reactivity of the precursors compared to the prior synthesis, we have demonstrated synthesis of PbS nanosheets with controllable thickness and shape. Ideally, nanocrystal surfaces would be terminated with atoms or molecules that passivate all surface defects while allowing strong electronic coupling of adjacent nanocrystals. We have shown that ligand removal by ammonium sulfide treatment, followed by iodine treatment, can produce improved surfaces by creation of a thin shell of lead iodide. When this treatment is applied to nanocrystals passivated by the combination of long oleate ligands along with cadmium and chlorine ions, the resulting films exhibit both reduced defect density and improved carrier transport compared to previous films. The films will be assessed in photovoltaic devices.

EARLY CAREER: Functional Domain Walls as Active Elements for Energy Technology

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Funding: \$150,000 (2014)

PROGRAM SCOPE

This project aims to understand and exploit novel physics and functionalities of domain walls in transition metal oxides for their use as active elements to direct matter and energy. Heterophase and homophase domain walls are mobile and nanoscale elements existing in a wide range of materials; they can host remarkable, emergent functionalities that are absent in the bulk. This may lead to a variety of new energy technologies that are superior to existing ones. The PI seeks to understand the fundamental mechanism governing diffusion and recombination of point defects facilitated by domain walls, demonstrate ultra-sensitive transduction of wind and heat based on domain wall motion, explore and exploit effects of domain walls in electrothermal transport for nanoscale thermal management, and finally probe the physical behavior of correlated electrons confined within domain walls as a quasi-two-dimensional electron liquid.

FY 2014 HIGHLIGHTS

(1) We developed a VO_2 nanowire-based microthermometer for quantitative evaluation of electron beam heating. This microthermometer can serve as a thermal flow meter to investigate sample heating from the incident electron beam inside electron microscopes. Owing to its small size the vanadium dioxide nanowire-based microthermometer has a large measurement range and high sensitivity, making it a good candidate to explore the temperature environment of small spaces or to monitor the temperature of tiny, nanoscale objects. Published at *Nature Commun.*, 5, 4986 (2014). (2) We directly observed nanoscale Peltier and Joule effects at metal-insulator domain walls in vanadium dioxide nanobeams. Published at *Nano Lett.*, 14, 2394(2014). (3) We discovered monolayer behavior in bulk ReS_2 due to electronic and vibrational decoupling. Such vanishing interlayer coupling enables probing of two-dimensional-like systems without the need for monolayers. Published at *Nature Commun.*, 5, 3252 (2014). (4) We demonstrated powerful, multifunctional torsional micro muscles activated by phase transition. These torsional muscles combine multiple functions as torsional actuators, micro catapults, proximity sensors, as well as memristors. Being able to sense a distanced object and then respond by rotating to a different configuration, the torsional muscles simulate active neuromuscular systems with all-inorganic materials. Published at *Adv. Mater.* 26, 1746 (2014). (5) We discovered a temperature-gated thermal rectification effect for active heat flow control using asymmetric VO_2 nanowires. To the best of our knowledge, this is the first demonstration of solid-state active-thermal devices with a large rectification ($\sim 20\%$) in the rectifier state. This temperature-gated rectifier can have substantial implications ranging from autonomous thermal management of heating and cooling systems to efficient thermal energy conversion and storage. Published at *Nano Lett.*, 14, 4867 (2014).

Delafossite Semiconductor Nanocrystals for p-type Dye-sensitized Solar Cells

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Funding: \$174,000 (2014)

PROGRAM SCOPE

A major challenge in developing efficient p-type dye-sensitized solar cells (p-DSCs) is the lack of p-type wide-bandgap semiconductors with good transparency and high hole mobility. Our prior results have clearly shown that CuGaO₂ holds a great promise as the p-type semiconductor in p-DSCs. Therefore, in this renewal project, we will systematically investigate Cu(I)-based p-type delafossite semiconductors including CuAlO₂, CuGaO₂ and CuScO₂. The goal is to understand the basic chemistry and crystallization process in the hydrothermal synthesis of these delafossite nanocrystals, determine their band energies, and measure the charge carrier dynamics at the semiconductor/dye/electrolyte interface. The results will be important not only for dye-sensitized solar cells, but also for other fields such as transparent electronics, organic photovoltaics and photoelectrochemical cells for solar fuels. The use of CuAlO₂, CuGaO₂ and CuScO₂ can overcome the limitations of the commonly used NiO in p-DSCs. (1) These delafossites do not have partially filled 3d orbitals, and thus are more transparent than NiO to the visible light. (2) These delafossites have significantly higher hole mobility than NiO. The top of valence band of CuAlO₂, CuGaO₂ and CuScO₂ is from the mixing of Cu-3d orbitals and O-2p orbitals that reduces the localization of the valence band edge. The high hole mobility in our proposed delafossites should have a profound effect on the kinetics of hole transport and recombination reactions in p-DSCs. The results from this renewal proposal will have an impact to the fundamental materials science of delafossites. The knowledge will establish an understanding of the crystallization of delafossite nanocrystals, and also the physical properties of the delafossite/electrolyte junctions. Moreover, these delafossites have the technologically important applications as the p-type transparent conducting oxides.

FY 2014 HIGHLIGHTS

A major achievement is the successful synthesis of CuGaO₂ nanocrystals based on our established understanding of its crystallization mechanism. This will pave the road for our subsequent research on CuGaO₂-based p-DSCs. We have also synthesized 7 new dye molecules for efficient hole injection in p-DSCs. Another interesting result is the generation of high cathodic photocurrents via sensitizing a degenerate n-type semiconductor: tin-doped indium oxide (ITO). This discovery was counter-intuitive, because dye-sensitized solar cells (DSCs) are majority carrier devices. Conventional wisdom uses n-type semiconductors for n-type DSCs and p-type semiconductors for p-type DSCs. Our dye-sensitized ITO electrode delivers a cathodic photocurrent as high as 5.90 mA cm⁻², which is close to the highest record for p-type DSCs. Ultrafast transient absorption spectroscopy studies indicate that the cathodic photocurrent results from reduction of the photoexcited sensitizer by free electrons in the conduction band of ITO. Our results reveal a new perspective toward the selection of semiconductors for sensitized photocathodes. This novel type of photoelectrode has promising applications in DSCs and solar fuels. Another result is about the concept of "solar battery", which is related to DSCs, but is outside the scope of my proposal. This work describes an interesting photo-assisted charging approach to address the overpotential challenge in Li-O₂ batteries. The novelty is in the use of a redox couple to integrate a dye-

sensitized photoelectrode with the oxygen electrode in a Li-O₂ battery. This is a unique way to utilize the solar energy to compensate the energy cost in the charging process. I am enthusiastic of this work. It shows an elegant example on how to use photoelectrochemical approaches to solve battery challenges, and represents a new direction in battery research.

Polymeric Multiferroic, Collaborative Research between University of Maryland and Kansas University

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Principal Investigator: Manfred Wuttig

Sr. Investigator(s):

Students: 0 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)

Funding: \$122,000 (2014)

The University of Kansas part of this project is listed separately under Principal Investigator: Shenqiang Ren

See the entry for “Collaborative Research: Polymeric Multiferroics” for the Program Scope and FY 2014 Highlights.

Enhancement of Magnetoelectric Coupling in Nanoengineered Oxide Films and Heterostructures by Laser MBE

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Principal Investigator: Xiaoxing Xi

Sr. Investigator(s):

Students: 0 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)

Funding: \$122,215 (2014)

PROGRAM SCOPE

The main focuses of the project are the (BaTiO₃)_n/(CaMnO₃)_n short-period superlattices, which have been predicted to exhibit interface-induced giant magnetoelectric coupling. BaTiO₃ is highly resistant to oxygen octahedral rotations, which suppress the MnO₆ octahedral rotation in CaMnO₃, leading to a ferroelectric ground state whose polarization depends strongly on the magnetic ordering. The enhancement of the magnetoelectric coupling is the strongest for the shortest superlattice period $n = 1$. This mechanism is different from the enhancement of magnetoelectric coupling by strain and charge mediation at oxide interfaces. It represents a new and novel paradigm in the search for strong multiferroic materials. The artificially built layered materials (BaTiO₃)_n/(CaMnO₃)_n superlattices will be grown by laser molecular beam epitaxy (MBE) from separate oxide targets. This approach is different from laser MBE practiced in the most other labs, where compound targets are used to grow films (for example, growing SrTiO₃ films from a SrTiO₃ target). In our research, targets of BaO, TiO₂, CaO, and MnO₂ will be used and ablated alternately to deposit one atomic layer at a time. For example, the basic sequence of the atomic layer deposition for a (BaTiO₃)₁/(CaMnO₃)₁ superlattice will be BaO- TiO₂-CaO- MnO₂, which repeats itself. We have demonstrated that the atomic layer-by-layer mode of the laser MBE growth is superior to the conventional laser MBE in achieving stoichiometry control and more suitable for the synthesis of the short-period superlattices in this project. The success of this project will further establish that laser MBE from separate oxide targets is capable of producing oxide thin films and

heterostructures with equally extraordinary quality as can be achieved by reactive MBE. Various structural, ferroelectric, and magnetic measurements will be performed to detect ferroelectricity, determine the magnetic ordering, and characterize the magnetoelectric coupling in these thin film samples.

FY 2014 HIGHLIGHTS

(1) Based on previous year's results, we have furthered the understanding and control of the atomic layer-by-layer growth by laser MBE from separate oxide targets via RHEED intensity oscillation, which has led to homoepitaxial SrTiO₃ films of better stoichiometry and crystalline perfection. In particular, RHEED intensity oscillations of nonstoichiometric SrTiO₃ layer followed by stoichiometric growth present double peak features, which is a very sensitive method to control the stoichiometric growth. (2) Using this growth technique, we have grown epitaxial LaAlO₃ films with different stoichiometry from La₂O₃ and Al₂O₃ targets on SrTiO₃. We have found that the interfacial layers are conducting for all LaAlO₃ film stoichiometry and the interfacial properties do not change with stoichiometry more than the doping effect, contrary to the published results claiming that Al off-stoichiometry is necessary for the formation of the 2D electron gas. (3) Using this growth technique, we have grown the Ruddlesden-Popper phase of La_{n+1}Ni_nO_{3n+1} with n=4 from La₂O₃ and Ni₂O₃ targets. This phase has not been grown by any other growth technique. The result demonstrates that this growth technique is a powerful tool for growing materials not possible for other growth techniques, important for materials by design. (4) Using this technique, we have grown epitaxial CaMnO₃ films from CaO and MnO₂ targets on different substrate. The electronic structure of the films measured by the polarization dependence x-ray absorption spectroscopy and hard x-ray photoemission spectroscopy shows extraordinary high film quality. The result lays the foundation for the growth of the (BaTiO₃)_n/(CaMnO₃)_n short-period superlattices.

Hetero-Junctions of Boron Nitride and Carbon Nanotubes: Synthesis and Characterization

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Funding: \$333,500 (2014-2016)

PROGRAM SCOPE

Co-axial hetero-junctions of boron nitride nanotubes (BNNTs) and carbon nanotubes (CNTs) are theoretically predicted to have appealing properties that are not available in pure BNNTs and CNTs. Experimental realization of these of BNNTs/CNTs junctions was hindered by the absence of common growth techniques for both types of nanotubes. During the previous funded project, we have obtained a breakthrough on controlled growth of BNNTs on substrates by catalytic chemical vapor deposition (CCVD) technique using Fe, and Ni catalysts. Since we have previously reported on the growth of single- and multi- walled (SW and MW) CNTs by CCVD using the same catalysts, a common route to grow BNNTs and CNTs on substrates is thus obtained. Based on this unique capability, this new research project will synthesize BNNTs/CNTs junctions by CCVD and investigate their unique physical properties. The nature of the project is very challenging, but will lead to cutting-edge sciences. The far reaching goal of this project is to grow desired BNNTs/CNTs junctions with tunable band structures and properties. Isolated and superlattices of these BNNTs/CNTs junctions are expected to be multi-functional, with

unique electronic, photonic, magnetic, and spintronic properties. Thus, BNNTs/CNTs junctions are important nanotubular structures for energy efficient device fabrication and application. Every devices fabricated by using BNNTs/CNTs junctions would be useful for multiple applications at the nanoscale. Finally, this project will also strengthen our current collaborations with multiple Department of Energy's Nanoscale Science Research Centers (NSRCs), including the Center for Nanophase Materials Sciences at Oak Ridge National Laboratory, and the Center for Integrated Nanotechnologies at Sandia National Laboratories and Los Alamos National Laboratory.

FY 2014 HIGHLIGHTS

The project was started on September 1, 2014. One graduate student and one postdoc are working on improving the uniformity of the Au quantum dots on the QDs-BNNTs. Two users proposals have also being submitted to the Center for Nanophase Materials Sciences (CNMS) at Oak Ridge National Laboratory to gain access to some needed facilities.

Tailoring Thermal Radiative Properties with Doped-Silicon Nanowires

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Funding: \$104,980 (2014)

PROGRAM SCOPE

A new kind of anisotropic metamaterial with a hyperbolic dispersion in a broad infrared region is proposed. It is based on aligned doped-silicon nanowire (D-SiNW) arrays, which are relatively easy to fabricate at the wafer scale. D-SiNW-based metamaterials have unique thermal radiative properties, such as broadband omnidirectional absorption whose width and location can be tuned by varying the filling ratio and/or doping level. Furthermore, extremely high figure of merit (FOM) can be achieved in a wide spectral region, suggesting that D-SiNW arrays may be used as a negative refraction material with much less loss than other structured materials, such as layered semiconductor materials. A combined theoretical and experimental investigation will be performed to characterize D-SiNW arrays for tailoring thermal radiative properties. Both the effective medium approximation (EMA) and finite-difference time-domain (FDTD) method will be used to study wave propagation, energy density, and radiation absorption in the inhomogeneous medium. Angle-resolved transmittance and reflectance measurements of fabricated samples will be performed using a Fourier-transform infrared spectrometer with different polarizations at wavelengths from 2 to 20 μm . Near-field thermal radiation between anisotropic materials with hyperbolic dispersions will also be predicted for potential application in energy harvesting. This project aims at realizing D-SiNW-based metamaterials for thermal radiation control as well as for near-field thermal imaging in the mid-infrared. It is well aligned with the PI's long-term goal of providing leadership and expertise in thermal radiation at the nanoscale for energy harvesting and infrared sensing applications. Furthermore, other metamaterials such as multilayered structures, periodic gratings, and graphene will also be investigated for near-field and far-field thermal radiation characteristics and applications.

FY 2014 HIGHLIGHTS

We have shown (Liu *et al.*, 2013, APL_103, 213102) that a vertically aligned carbon nanotubes array can enhance near-field radiation through the hyperbolic modes. A number of different nanostructures containing doped Si are shown to enhance near-field heat transfer over bulk doped-Si, such as doped-Si nanowires (D-SiNWs), doped-Si nanoholes (D-SiNHs), multilayered metamaterials, and D-Si gratings (Liu *et al.*, 2014, IJHMT_73, 389). Recently, we obtain the energy streamlines through two semi-infinite uniaxial anisotropic effective medium structures, separated by a vacuum gap (Bright *et al.*, 2014, Opt. Express_22(S4), A1112). This work offers an estimate of the critical lateral dimension. We have also investigated the validity of the effective medium theory (EMT) in predicting the near-field radiative heat transfer between multilayered metamaterials. Combining the Bloch theory with the cutoff wavevector, the application condition of EMT is presented and verified (Liu *et al.*, 2014, JHT_136, 092703). Graphene has attracted great attention in nanoelectronics, optics, and energy harvesting. We have investigated the near-field radiative heat transfer between graphene-covered corrugated silica based on the exact scattering theory (Liu and Zhang, 2014, APL_104, 251911). Graphene can improve the radiative heat flux between silica gratings by more than an order of magnitude, suggesting possibilities for more efficient thermal management and photon energy harvesting. Furthermore, by combining graphene plasmons and hyperbolic modes, we have demonstrated photon tunneling with near-unity probability across a broad frequency range and large wavevector space (Liu *et al.*, 2014, ACS Photonics_1, 785). It is found that near-field heat transfer coefficient between D-SiNWs can be improved further (by several folds) when covered by a graphene sheet, thanks to the hybridization of graphene plasmons and broadband hyperbolic modes.

DOE National Laboratories

EARLY CAREER: Light-Stimulated Epitaxy of Novel Semiconductor Alloys and Heterostructures

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Funding: \$500,000 (2014)

PROGRAM SCOPE

The primary objective of this project is to investigate the influence of photons on the growth of semiconductor thin films by molecular beam epitaxy in order to 1) improve our basic understanding of growth mechanisms, 2) selectively stimulate and manipulate processes that lead to atomistic growth control and 3) advance the synthesis and investigation of novel semiconductor alloys and heterostructures. Continuing to push the boundaries of synthesis through the exploration of radically new approaches tailored to deliberately alter or enhance specific growth processes will be a key factor in overcoming longstanding synthesis challenges that pose a barrier to materials research. Light offers the unique ability to modify growth processes through the selective injection of energy into the surface of a growing film and the photogeneration of carriers. Studies specifically focus on exploring the basic mechanisms through which photons affect adatom mobility, bonding, the incorporation of alloying species and interface formation at low growth temperatures. This information is used to tailor the growth of new semiconductor alloys and heterostructures that are difficult to synthesize by traditional

techniques. Once synthesized, the properties of these new materials and heterostructures are explored for use in energy-related applications, such as photovoltaics and solid-state lighting.

FY 2014 HIGHLIGHTS

We have determined several mechanisms by which photons and photogenerated carriers affect growth processes. The influence of light stimulation on adatom migration was probed by in-situ measurements of the layer-by-layer to step flow growth mode transition. Contrary to previous understanding, our measurements showed that the adatom diffusion length in GaAs actually decreases under illumination. Surface morphology measurements with atomic force microscopy (AFM) also show that broadband illumination roughens the surface. We have attributed these changes to the blocking of adatom attachment sites at step edges by photogenerated carriers, which is similar to the reported role of hydrogen in GaAs growth. Additionally, we have shown that photogenerated carriers can be used to tune the Fermi energy during growth and suppress undesired growth processes driven by Fermi level pinning. Movement of the Fermi energy away from the Fermi stabilization energy as well as Fermi level pinning are known to significantly influence dopant incorporation and diffusion, defect formation, surface reconstruction and growth processes governing surface morphology. Our experimental measurements of n and p-type doped GaAs demonstrate that photon irradiation during growth reduces surface segregation and migration of dopants. These results are explained on the basis that splitting of the quasi Fermi levels by the photogeneration of carriers reduces the surface electric field and the formation of defects, which facilitate dopant atom drift and diffusion, respectively. These results suggest that light stimulated epitaxy techniques can be used to improve the growth of highly doped structures with reduced thicknesses. This information will also serve as a guide to the ongoing investigation of light stimulated growth of II-VI semiconductors and heterostructures.

EARLY CAREER: Spatially Resolved Ionic Diffusion and Electrochemical Reactions in Solids

Institution: Oak Ridge National Laboratory
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Funding: \$500,000 (2014)

PROGRAM SCOPE

The functionality of energy storage systems, such as Li-ion batteries, is based on and ultimately limited by the rate and localization of ion flows through the device on different length scales ranging from atoms over grains to interfaces. The fundamental gap in understanding ionic transport processes on these length scales strongly hinders the improvement of current and development of future battery technologies. The goal of this proposal is to create, through nanometer-resolution imaging of ionic flows, fundamental understanding of the local mechanisms which define a rechargeable battery. Using Electrochemical Strain Microscopy, which utilizes the intrinsic link between unit cell volume and Li-ion concentration, it is possible to separate and characterize transport processes in the electrodes and across electrode/electrolyte interfaces, allowing us to decipher the single stages of ionic transport through the battery. With this knowledge it will be possible to identify and overcome the bottlenecks which lead to predominant limitations in present battery technology such as low energy storage density or capacity loss during cycling. The success of this proposal will propel ORNL, both directly and through

collaborative teams, into a highly competitive position for new DOE energy research and development centers, as well as EERE and DOE BES programmatic support.

FY 2014 HIGHLIGHTS

Several signal generating mechanisms need to be considered during standard scanning probe based characterization techniques in order to get closer to quantification of localized ionic transport through electrochemical strain microscopy (ESM) measurements. ESM was developed to detect ionic transport with nanometer resolution using strain, generated through ion concentration changes, to explore structure-functionality relationships in Li-ion battery cathodes and anodes. During ESM, the local ion concentration can be changed by applying a bias to the Scanning Probe Microscopy (SPM) tip in contact with the sample and the ionic transport is detected through changes in sample volume based on the Vegard law which correlates ionic concentration and unit cell volume. Due to the nature of this experiment, not only Vegard-type volume changes, but also other electrochemical processes happening in the probed volume can contribute to the measured ESM signal, e.g. the formation of chemical dipoles. Therefore, it is crucial to discuss and explore all phenomena happening under the biased SPM tip. We identified these processes and, based on their dependences on sample and experimental parameters, developed experimental techniques to differentiate between them. This is not only crucial for ESM but for any other type of SPM technique where local electrical biases are applied, e.g. ferroelectric materials. These new experimental measurement concepts were then tested on a variety of material classes. In addition to the standard cathode and anode materials for Li-ion batteries, we also explored the reversibility of Li-ion motion in previously unexplored solid electrolytes. Here, the biased SPM tip can locally extract Li-ions from the electrolyte and form Li-metal on the sample surface. The kinetics and reversibility of this phenomenon were studied. Working on all elements of the battery will give us a better picture of all processes relevant for battery operations.

Light-Matter Interaction Phenomena using Subwavelength Engineering of Material Properties

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Students:	5 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	\$950,000 (2014)

PROGRAM SCOPE

The project goal is to obtain a fundamental understanding and control of light-matter interaction through engineering material properties at the subwavelength scale. Our approach involves using both localized and propagating metamaterial photon modes coupled to semiconductor heterostructures. The metamaterials allow tailoring the photonic mode properties, while the semiconductor heterostructures enable the creation of electronic and vibrational transitions with desired characteristics. The ultimate goal is to control the flow of energy between photons, phonons, and electrons in ways that are not possible with natural materials. One thrust will investigate strong coupling of the localized modes of planar metamaterial nanocavities and other plasmonic structures to semiconductor transitions. The

ultra-small volume of the localized resonant “cavity” modes of the metamaterial resonators, along with the ability to tailor the near-field overlap with the adjacent semiconductor structures enable the exploration of strong light–matter coupling in this technologically relevant system. Achieving such coupling could offer new ways to control processes that depend on electron-phonon scattering, create new record optical nonlinear materials or novel emitters at infrared wavelengths, and create condensates of excitons without the use of complex microcavities. A second thrust will explore the coupling of the propagating modes of hyperbolic metamaterials to semiconductor transitions when absorber/emitters are embedded within semiconductor superlattice hyperbolic metamaterials. The hyperbolic isofrequency surfaces of these deep subwavelength metamaterials lead to unusual electromagnetic mode behavior such as broadband enhanced density of propagating states and very large photon momentum. This can profoundly alter light–matter interactions and could be used for the design of advanced absorbers and emitters for energy conversion, lighting applications, and single photon sources.

FY 2014 HIGHLIGHTS

Previous attempts at increasing the strong light-matter coupling between metamaterial and plasmonic nanocavities and different types of emitters or solid-state excitations with a dipole moment, focused mainly on the properties of the two-level system while ignoring the effect of the metamaterial geometry. In this fiscal year, we demonstrated experimentally that the strong light-matter coupling can be described by a simple equivalent circuit model and that the electrostatic capacitance of the single metamaterial nanocavity is the crucial parameter determining the coupling. We made progress in the understanding and use of epsilon-near-zero modes. These modes arise in very thin layers when the permittivity is close to zero and they are characterized by a nearly flat dispersion. We proved that these modes are long-range plasmons for layers much thinner than the skin depth. These modes lie to the right of the light line and are related to the Berreman modes, which lie to the left of the light line. In a different but related work, we used Berreman modes in very thin highly doped semiconductor layers to create narrowband thermal emission, when the samples were heated. We have performed full wave simulation and analytic modeling of semiconductor hyperbolic metamaterials (SHMs), and have compared their performance to metal-based hyperbolic metamaterials. We find that the combination of small layer thicknesses and infrared operating wavelengths allows the SHMs to achieve much larger photon momentum states than are achievable with the metal based systems. This, in turn, should lead to much larger densities of states and much larger emission enhancements. We have also designed and initiated growth of a set of SHMs on which we will fabricate metallic metamaterial resonators and demonstrate strong coupling to the longitudinal resonance of the hyperbolic permittivity.

Characterization of Functional Nanomachines

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 Students: 2 Postdoctoral Fellow(s), 3 Graduate(s), 0 Undergraduate(s)
 Funding: \$911,000 (2014)

PROGRAM SCOPE

The goal of this program is to understand the fundamental principles of nanomachine systems and to apply those principles toward the creation of new nanomachines capable of converting energy into directed mechanical action at the nanoscale. We seek to understand the microscopic mechanisms underlying nanomechanical processes in both synthetic and naturally occurring nanomachines that operate in different dissipative environments.

FY 2014 HIGHLIGHTS

First atomically-resolved imaging of polymerization at a surface via Bergman cyclization has enabled microscopic determination of single-polymer chemical and electronic structure. This has provided insight into a new microscopic coupling mechanism for surface molecules. Infra-red scanning tunneling microscopy (IRSTM) spectra were quantitatively modeled for the first time. This demonstrates that IRSTM is a viable new tool for simultaneously determining atomic-scale molecular structure, intermolecular interactions, and substrate coupling for adsorbed molecules. Single-molecule laser-tweezer methods were used to show that RNA polymerase dynamics conform to a linear Brownian ratchet model. This provides important new understanding of how molecular-machine behavior regulates biological gene expression. A new technique has been developed to fabricate high quality graphene resonators using polymer-free, direct transfer onto carbon grids. Fabry–Perot interference of the resonators was used to determine graphene's intrinsic bending rigidity.

Proximity Effects in Charged Oxide Heterostructures

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Funding: \$1,272,000 (2014)

PROGRAM SCOPE

The mission of the Proximity Effects in Charged Oxide Heterostructures program is to fundamentally understand and thereby control defect behavior in oxide heterostructures. We perform *in situ* synchrotron x-ray studies of thin film synthesis and heterostructure behavior in controlled environments, complemented by first-principles simulations and multiscale computational theory to reveal the effects of interfacial proximity on defect behavior and the resulting electrochemical properties. In recent years, it has become clear that many of the remarkable properties discovered in the field of complex oxide heterostructures may be related to charged defects and their behavior at interfaces. Such phenomena, however, remain poorly understood due to the inherent difficulties in probing defect-interface interactions at the atomic-level and in the environments relevant to defect evolution. We address this problem by growing heterostructures with precise cation ordering and variable oxygen concentrations, enabling the systematic investigation of defect formation and migration

behavior both during synthesis and while processing in different electrochemical environments. Throughout this program, the atomistic results are fed back to computational theory to gain insight into the mechanisms and the electronic and energetic processes taking place during defect structure evolution. Through this combined *in situ* x-ray / computational theory approach, our ultimate goal is to form a knowledge-basis of defect behavior, which will be analyzed for the discovery of descriptors that can enable large-scale predictions of interface-dependent defect transport kinetics and provide new insight for the design and synthesis of materials with tailored, tunable, and multifunctional defect-engineered properties.

FY 2014 HIGHLIGHTS

We grew layered films by oxide MBE, finding that although MBE permits growth with atomic level control, the layers can rearrange themselves dynamically during deposition. This can lead to significant roughening of the growth surface and a general loss of vacancy ordering. These *in situ* x-ray results were obtained using the world's first oxide MBE system on a synchrotron beamline at Sector 33 of the Advanced Photon Source. Results were published in Nature Materials. Through in-situ X-ray studies, we determined the effects of substrate surface polarity on the ferroelectric-to-paraelectric phase transition behavior of PbTiO_3 films grown on a polar surface of DyScO_3 . The electrical boundary conditions imposed by the substrate surface result in significant T_C suppression and different domain structures in films with and without non-polar insulating or conducting intermediate layers. Results were published in Applied Physics Letters. We used an *in situ* x-ray approach to study SrRuO_3 single crystal films, finding that the activity for the oxygen evolution reaction (OER) depends on surface orientation. The Ru cation oxidation state increased during the OER, followed by significant surface roughening. This was the first demonstration of the inverse relationship between activity and stability for oxide systems, and points out the need for new materials that strike the proper balance between activity and stability. Results were published in Nature Communications. We investigated oxygen octahedral tilt transitions and tilt structures in $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructures, finding that the tilt transition temperature for LaAlO_3 was significantly elevated with respect to the bulk and depends on film thickness. These results indicate that most LaAlO_3 films undergo an irreversible tilt transition when cooling from the deposition temperature, with a resulting domain structure and average tilt angle that depends on thickness as well as strain. Results were published in APL Materials.

Atomistic and Mesoscopic Study of Metallic Glasses

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Funding: \$974,000 (2014)

PROGRAM SCOPE

The goal of this project is to gain fundamental understanding of the science of metallic liquids and glasses and to develop a theory that is capable of guiding the experimental development of new bulk metallic glasses (BMG) with superior properties. Because of the strongly disordered atomic structure metallic glasses have exceptionally high strength. The recent development of BMG has greatly improved

the potential for application of metallic glasses as a structural material. However, the basic science of metallic glasses at the atomistic level remains poorly developed. As a consequence, the experimental effort to develop new BMG is largely guided by empirical principles and intuition. This difficulty originates from the fact that in the liquids and glasses atoms are strongly correlated in spite of the apparent disorder in the structure, and to describe such a structure we directly face the many-body problem. In this program we seek fundamental understanding of atomistic mechanisms which control the structural and dynamic properties of metallic liquids and glasses through combination of tightly coupled simulation, theory and experiment. To overcome theoretical difficulty we use a novel approach, based upon the concept of fluctuations in the local topology of atomic connectivity network. The computational effort includes classical as well as first-principles calculation molecular dynamics (MD) simulation. Experimental studies include synchrotron x-ray and neutron scattering and nanoscale mechanical testing. Our plan is to create guiding principles of BMG formation and deformation through this study, leading to the development of metallic glasses with superior properties. This will be accomplished by making full use of excellent scientific and technical expertise of the co-PI's and the PI, and outstanding facilities at ORNL and other DOE laboratories, including the Spallation Neutron Source (SNS) and the high-speed computers at ORNL.

FY 2014 HIGHLIGHTS

In FY 2014 we made significant advances in understanding various fundamental aspects of mechanical deformation in metallic glasses. (1) We showed that mechanical deformation in metallic glasses is triggered by a small group of atoms, involving just five atoms on average. This was achieved through the use of the activation-relaxation technique to detect the saddle point in the potential energy landscape. This result represents an important breakthrough because it shatters the myth that some highly collective process is involved in deformation in metallic glasses. (2) We also discovered a structural signature of ductility. Metallic glasses are promising as structural materials because of their extremely high strength, but most of them have small, or no ductility, which severely limits their application. We discovered that the structural response to elastic loading which can be detected by x-ray diffraction is related to ductility. This is a major development, because we now have a clue as to improve ductility. We hope to develop new, more ductile, metallic glasses using this finding as a guide. (3) We succeeded in characterizing the structural heterogeneity of metallic glasses through nanomechanical testing, and in describing the structural heterogeneity in terms of defect strength and distribution. We found that the effective defect density drops significantly with the structural relaxation, and the fracture of metallic glasses changes from a significantly plastic mode to an extremely brittle one. (4) Finally we have calculated the energy landscape of metallic liquids at high temperatures and demonstrated how it can elucidate the properties, such as viscosity and relaxation time. The concept of potential energy landscape (PEL) is a powerful approach, but it is very difficult calculate, or even to visualize, the actual PEL. We proposed the new concept of local energy landscape (LEL) and successfully applied it to high temperature metallic liquids.

Solar Energy Research Institute for India and the United States (SERIUS)

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Reuben Collins; Colorado School of Mines
Rakesh Agrawal; Purdue University
Suresh Garimella; Purdue University
Ashraf Alam; Purdue University
Mark Poliks; New York-Binghamton, State University of

Students: 5 Postdoctoral Fellow(s), 8 Graduate(s), 0 Undergraduate(s)

Funding: \$1,250,000 (2014)

Jointly funded by the Chemical Sciences, Geosciences, & Biosciences Division and Materials Sciences and Engineering Division

PROGRAM SCOPE

This research consortium, co-led by the Indian Institute of Science-Bangalore and the National Renewable Energy Laboratory, sets out to create an environment for cooperation and innovation “without borders” to develop and ready emerging and revolutionary solar-electricity technologies toward the long-term success of India’s Jawaharlal Nehru National Solar Energy Mission and the U.S. DOE SunShot Initiative. SERIIUS carries out fundamental and applied research, analysis and assessment, outreach, and workforce development through specific bi-national projects in three research thrusts: (1) Sustainable Photovoltaics (PV) to develop next-generation materials, devices, and advanced manufacturing processes tailored to the needs, environment, and resource availability of India and the US; (2) Multiscale Concentrated Solar Power (CSP) to overcome critical science and engineering challenges for reliable multiscale (including small 25–500 kW) CSP systems; and (3) Solar Energy Integration (SEI) to identify and assess key technical, economic, environmental, and policy barriers, enabling a research agenda for technical readiness in India and of benefit to the U.S. SERIIUS has created a bi-national network for fostering new ideas and collaborations to expedite a sustainable industry. SERIIUS is developing disruptive technologies through foundational research in PV and CSP to address the critical barriers for solar energy development in India that intersect the grand challenges for solar energy in the U.S. SERIIUS is jointly funded under the Joint Clean Energy Research and Development Center (JCERDC) through the U.S. DOE and the Government of India over a 5-year period (starting October 1, 2012). The Consortium is also supported by cost share from its members. The Consortium comprises 32 partners from India and the U.S.; further information on these organizations and specific SERIIUS activities is available on its website: www.SERIIUS.org.

FY 2014 HIGHLIGHTS

Photovoltaic Thrust: • Development of new polymers for dye-sensitized solar cells (DSSC) and organic photovoltaics (OPV) based on starting molecule computational analysis, and initial device development and subsequent testing across the team. • Initial CZTS electrodeposition showed correct phase formation without hydrazine on Willow Glass; nanoparticle-based CIGS resulted in meaningful efficiencies. • The electroluminescence technique was developed as a tool to evaluate heterojunction with intrinsic thin layer (HIT) solar cells. Tests on initial 1-cm² and subsequent 25-cm² samples were accomplished. Initial results demonstrate that this can be an important basic diagnostic for HIT and other solar cells. • Developing a comprehensive database for insolation and reliability vs. climate across

India to provide a basic understanding of resource availability and failure modes in order to produce mitigation strategies for this significant Indian problem. • Developing an understanding of the dust and soiling problems in India and the development of coatings-based mitigation strategies. • New nano-hybrid encapsulation technology gives very low water vapor transmission rate (WVTR). Multiscale Concentrated Solar Power Thrust: • Optimization and engineering models for new scalable systems using CO₂-based Brayton (high temperature) and organic-based Rankine cycles (low temperature) have produced new technology-specific designs that are now under construction. • A new turboexpander is being fabricated and will be evaluated in a new test bed for high-temperature Brayton cycle. • A tubular serpentine receiver was designed; CFD model predicts an efficiency > 74%. • New Earth-abundant high-performance reflector and absorber coatings developed. • New low-cost heliostats have been developed at very low capex and are begin tested. Solar Energy Integration Thrust: • Analysis of policies and techno-economics of grid-connected PV in India Roadmap • Draft Roadmap for Energy Storage for India was developed. • Technology improvement opportunities for PV and CSP thrusts are being defined.

Electronic Materials Programs

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 Junqiao Wu; Lawrence Berkeley National Laboratory
 Students: 1 Postdoctoral Fellow(s), 5 Graduate(s), 0 Undergraduate(s)
 Funding: \$1,646,000 (2014)

PROGRAM SCOPE

Electronic Material Program (EMAT) discovers and creates semiconductors of novel composition and morphology for energy applications by removing chemical and physical constraints that limit materials performance and growth. The program has three thrust areas: (1) Semiconductor quantum membranes: Spatial confinement, probing, and functionalization; (2) Band structure and interface tuning on command: Engineering band structures in semiconductor alloys, and electronic and structural properties at interfaces; (3) Control of phase transitions at the nanoscale. Common to these research themes is a synthetic strategy that allows us to control structure and phase transitions at the nanoscale. In the case of quantum membranes, our ability to make and control free-standing 2-D semiconductors enables study of the interplay of quantum confinement and surface/interface properties with electronic structure and carrier transport at a fundamental level. Our control of materials composition via highly non-equilibrium synthesis techniques allows us to tune band structures and interface properties on command. By exploiting new insights in the nanoscale control of phase transitions, we can synthesize new functional structures.

FY 2014 HIGHLIGHTS

We have developed a new growth mode for semiconductor thin films using the vapor-liquid-solid (VLS) technique (Scientific Reports, 2013). As a proof of concept, InP thin films are grown on non-epitaxial substrates (e.g., metal foils or amorphous glass) using the thin-film VLS process with an ultralarge grain size of up to ~ 1 mm and optoelectronic properties (including luminescence yield) approaching those of epitaxially grown layers. We also developed the nucleation and growth theory for this new mode of material synthesis. The work presents a promising route for low-cost growth of high quality III-V semiconductors for PV applications and beyond. In another project, we made the first experimental observation of spatially indirect transitions in heterobilayer transition metal dichalcogenides. Understanding where excitons are generated and recombined in heterobilayers presents the basis for any work done in this field. Our work clearly presents an important advance in this regard (PNAS, 2014). In addition, we reported the first experimental demonstration of indirect to direct band gap transition in 2D semiconductor multilayers using WSe_2 as a material platform (Nano Letters, 2014). This presents an important finding since the multilayers of most transition metal dichalcogenides are indirect band gap, limiting their application for optoelectronic devices. The research output of the program has resulted in over 30 journal publications since last year (including PNAS, Nature Materials, Nature Communications, Scientific Reports, PRB, Nano Letters), 11 of which are co-authored by multiple EMAT PIs.

Superconducting Materials

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Funding: \$692,000 (2014)

PROGRAM SCOPE

This program studies basic relationships between nanostructures and the macroscopic properties of superconductors. Both basic understanding and understanding of materials aspects for practical use are sought. Emphasis is on raising the critical temperature, T_c , and the critical current density, J_c , because they determine the limits to energy applications. Research activities focus on the responses of superconductivity and critical current to chemical, structural, and defect tuning in two classes of superconductors: (1) iron chalcogenides, and (2) cuprates. The key to increasing J_c is in controlling the pinning of magnetic vortices by defects in superconductors. In this program, defects are introduced precisely by controlled growth and ion irradiation. The goal is to create a landscape of tailored defects of desirable morphology and dimensions in superconductors that can produce the most effective vortex pinning in a broad range of temperatures and magnetic fields. Majority of materials are synthesized in thin film forms using an advanced pulsed laser deposition system capable of atomic layer-by-layer growth, and subsequently characterized via a range of techniques including transport, magneto-optical imaging, electron and optical spectroscopy, transmission electron microscopy, scanning tunneling microscopy, among others. We seek to understand and control the transport properties of superconducting materials by tackling a few key science issues, from the macroscopic to the atomic levels. Progress in the understanding of these two classes of materials could provide new strategies for enhancing T_c and designing new superconductors capable of enduring high magnetic fields and carrying high currents.

FY 2014 HIGHLIGHTS

We found post-annealing of a polar (001) Ceria surface can produce stable surface reconstructions, which have markedly different surface activities for the growth of iron-chalcogenide and cuprate thin films on CeO₂ buffered substrates. YBa₂Cu₃O₇ film grown on (001) CeO₂ surface having the longest, fourfold period, reconstruction exhibits a twofold increase in critical current density over surfaces with shorter period reconstructions. These findings opened a new avenue for catalysis mediated solid state synthesis of new complex materials. Iron chalcogenide (FeSe_{0.5}Te_{0.5}) thin films made with CeO₂ buffer are found to have both record high critical temperature and critical current density J_c under high magnetic field. Through proton irradiation, we achieved several fold enhancement of J_c . Furthermore, the films made on CeO₂ buffered bi-axially aligned flexible metal substrates have similar high performance to those made on CeO₂ buffered single crystalline. These studies demonstrated the potential of iron-based superconductors for energy applications. Grain boundary junctions were fabricated in the epitaxial FeSe_{0.5}Te_{0.5} thin films on [001] tilt SrTiO₃ bi-crystal substrates. Critical current densities across the junctions with different mis-orientation angles were measured at magnetic fields up to 30 T. A critical mis-orientation angle of a 9 degree was identified that separates the strong coupling region from the weak link region. The critical current densities across the grain boundary with a 24 degree mis-orientation angle can be modulated by the magnetic field, indicating a Josephson Effect that may be used for superconducting electronic applications where grain boundary Josephson junctions are required.

Field-Structured Composites

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Funding: \$115,000 (2014)

PROGRAM SCOPE

This project is focused on creating vorticity in dilute particle suspensions by subjecting them to multiaxial magnetic or electric fields. These induce flows can create highly effective heat and mass transfer, fluid mixing, and biomimetic fluid dynamics.

FY 2014 HIGHLIGHTS

We have discovered two countably infinite classes of fields that can induce vorticity: symmetry-breaking rational fields and rational triads. Symmetry-breaking rational fields are comprised of two orthogonal field components whose frequencies form a ratio that is rational and a third mutually orthogonal field component that is dc. Using number theory and set theory we have developed an analytical theory that is able to predict the direction of the fluid vorticity for any given frequency ratio, as well as the dependence of this vorticity on phase and sign of the dc field. A similar theory has been developed for rational triads, but in this case all three orthogonal field components are alternating. We have used these complex fields to create a variety of striking biomimetic dynamics. All of these results are published in Soft Matter, resulting in two invited journal covers.

Electronic Processes in Solid State Organic Electronic Materials

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Funding: \$221,000 (2014)

PROGRAM SCOPE

The central goal of this program is to advance our understanding of the fundamental physical principles controlling the behavior of organic electronic devices, and how these principles determine the performance in known and newly proposed devices. We focus our attention on the following fundamental questions: (i) How does molecular structure control the morphology, and charge and energy transport properties of condensed phases of organic materials, particularly at organic/inorganic and organic/organic interfaces? (ii) How are the electronic and optical properties of the interfaces affected by the presence of appropriately tailored molecules? (iii) In what way does this control the subsequent fundamental properties such as exciton dissociation, exciplex recombination, charge transport and energy transport at the interface?

FY 2014 HIGHLIGHTS

In the final year of this project we wrapped up our investigations of charge transfer effects at organic/organic and organic/inorganic interfaces in order to bring the program to a close. Our efforts addressed a number of issues, ranging from the 'Effect of Packing on Formation of Deep Carrier Traps in Amorphous Conjugated Polymers' (Kilina, *et al.*) to the formulation of "Interface Design Principles for High Efficiency Organic Semiconductor Devices" (Nie, *et al.*) Significant progress was also made in measuring and modeling the effect of a magnetic field on the electroluminescence of organic light emitting devices (Crooker, Liu, *et al.*).

Electronic and Optical Processes in Novel Semiconductors for Energy Applications

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Funding: \$1,230,000 (2014)

PROGRAM SCOPE

Advanced energy technologies require high-performance materials, which in photovoltaics (PV) translates to new semiconductor materials to efficiently absorb sunlight, and in solid-state lighting (SSL), to new semiconductor alloys for direct conversion of electricity to white light. A goal of this project is

fundamental materials research for the realization of semiconductors that transcend the existing limitations that constrain present PV and SSL technologies. It specifically addresses the current unavailability of efficient high bandgap (2.1 eV) and low bandgap (1 eV) absorbers for PV, and efficient amber emitters for SSL, via technologies based on GaAs substrates. The key to transcending the present limitations is understanding and controlling fundamental electronic and optical processes in semiconductor alloys, which is another goal of this project. Towards this, the project will focus on understanding the phenomena of spontaneous ordering in high bandgap lattice-mismatched AlInP, and the abnormal electronic structure and properties of isoelectronic dopants N and Bi in GaAs. Additionally, it will address recent observations of new excitations in photogenerated bipolar plasmon gasses, so as to achieve an understanding of collective phenomena that could enable semiconductors with novel, useful properties. Through collaborative efforts, this project utilizes the high-magnetic field facility at the NHFML (Los Alamos) and growth facilities at the CINT (Sandia labs).

FY 2014 HIGHLIGHTS

(1) We have successfully grown high quality epitaxial films of the dilute alloy dilute GaAsBi on GaAs substrates using a new MBE system. This is key to demonstrating the phenomenon of isoelectronic codoping of Bi and N into GaAs with the goal of regularizing the abnormal properties of the dilute alloy. Success in meeting this goal will have a profound impact in enabling the design of high efficiency multijunction solar cells grown lattice-matched to GaAs substrates in contrast to current technologies that are based on lattice-mismatched and lift-off approaches that are significantly more complex and expensive. (2) For almost four decades there has been an ambiguity concerning the precise value for the direct-to-indirect crossover in AlInP and AlGaAs with different values reported in various handbooks. Since this is of critical importance in the design of solar cell and LEDs, we precisely determined this crossover in both AlInP and AlGaAs semiconductor alloys using a very novel approach. (3) A new technique was developed to study long-range exciton diffusion in semiconductor material and applied to polycrystalline CdTe as well as single crystal CdTe which are at the forefront of current photovoltaic technologies, to show how carrier transport in these materials is influenced by defects and grain boundaries. (4) Results using femtosecond laser pulses to generate coherent acoustic phonons in the dilute Bismide alloy GaAsBi suggested that the incorporation of Bi in GaAs causes an enhancement of the hydrostatic deformation potential because of the resonant state in the valence band due to isolated Bi impurities. (5) A magnetically driven indirect-to-indirect crossover in AlGaAs was demonstrated using the NHMFL facilities at LANL. (6) Using the NHMFL facilities at LANL the effect of alloy statistical fluctuations on electronic properties of AlGaAs semiconductor alloys were investigated and its role in the direct-indirect crossover elucidated.

Complex Hydrides - A New Frontier for Future Energy Applications

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Funding: \$528,000 (2014)

PROGRAM SCOPE

Every energy-related application of hydrogen (H₂) requires safe and efficient storage. H₂ can be stored as a compressed gas, a cryogenic liquid, or in an H-rich solid. The first two approaches require substantial energy for compression or liquefaction, and, therefore, entail multiple containment, safety, and economical issues. Conversely, H-rich solids are believed to be the best medium to store high-purity H₂ required for fuel cells. Solid hydrides ensure high volumetric density of the fuel because in many of them the volumetric density of H₂ at ambient conditions is nearly twice that of a cryogenic liquid at 20 K, reaching 120 g H₂/l. The specific objectives of this FWP are to address issues that will advance basic science of complex hydrides and open up possibilities for their future use by drawing on the experience and expertise of principal investigators in materials science, physics and chemistry of complex hydrides, X-ray diffraction (XRD), high-resolution solid-state nuclear magnetic resonance (NMR), electron microscopy, and first-principles theory and modeling.

FY 2014 HIGHLIGHTS

A successful strategy for the solvent-free, room temperature mechanochemical synthesis of alane (AlH₃) via a solid state metathesis reaction of LiH and AlCl₃ has been developed. Alane, one of the forefront materials for practical solid-state hydrogen storage, has a hydrogen capacity of 10% by weight and gives up hydrogen in a single step at the temperature that is close to the operating temperature of hydrogen fuel cells. Prior to this work, realizing the enormous potential of alane has been frustrated by the lack of a straightforward method for its synthesis. The novelty of the process is the addition of AlCl₃ to the reaction mixture in three steps, hence completely suppressing parasitic side reactions that lead to a nearly complete loss of hydrogen from the system. By adding AlCl₃ to LiH in three steps and applying gas pressure, quantitative yield of AlH₃ – an important energetic material – has been achieved. X-ray diffraction, solid state NMR, and temperature programmed desorption analyses importantly established the mechanism of mechanochemical transformation: $3\text{LiH} + \text{AlCl}_3 \rightarrow 3\text{LiCl} + \text{AlH}_3$. This quick and efficient production method meets DOE requirements for hydrogen storage applications pending development of an economical large-scale synthesis process.

Extraordinary Responsive Magnetic Rare-Earth Materials

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Students:	1 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding:	\$1,125,000 (2014)

PROGRAM SCOPE

Responsive systems, where a small change of an extrinsic thermodynamic variable, such as temperature, pressure, or magnetic field, triggers an intrinsic phase change, have both fundamental and technological significance. Alloys and compounds that exhibit strong field-, temperature-, or pressure-controlled reactions, tunable by chemistry, crystallography, and processing, provide broad benefits to energy-related applications, such as sensors and smart materials, and materials for energy conversion, generation, and utilization devices. Responsive materials, therefore, have the potential to make

transformative changes that can be used to help meet our Nation's future energy demands. Conventional (and strong) stimuli are temperature and pressure, but a magnetic field is weak and often an underappreciated trigger, whose role in initiating strong changes in solids is much less understood. Knowledge of the mechanisms delivering minor-stimulus driven phase change that is then followed by a major perturbation of properties is crucial for guiding the discovery of new materials, and is the focus of this research. Our goal is to uncover the underlying electronic, atomic and microscopic interactions that result in an extraordinarily strong coupling of the magnetic and crystal lattices in chosen model systems representing rare earth-based intermetallic materials. Development and validation of phenomenological models of transformations that range from magneto-volume to magnetic-martensitic is one of our prime objectives.

FY 2014 HIGHLIGHTS

Combining a light and a heavy lanthanide leads to unique magnetism in a single material and in FY 2014 an unusual coexistence of ferro- and ferrimagnetism, metamagnetism, Griffith phase, and large exchange bias has been discovered in $\text{Pr}_{0.6}\text{Er}_{0.4}\text{Al}_2$. The material undergoes a trivial ferrimagnetism to paramagnetism transition in a zero magnetic field, but it exhibits multiple functionalities in magnetic fields greater than 40 kOe. Integrated experimental and theoretical study indicates that the underlying physics results from opposite signs of first and second nearest neighbor interactions, crystal field splitting, and magnetic instability related to effectively spherical average 4f charge density distribution. Additionally, the complex magnetic structure of Gd_5Ge_3 has been investigated by neutron powder diffraction down to 3.6 K. The primary antiferromagnetic ordering occurs at 82 K and produces a magnetic cell that is tripled with respect to the underlying orthorhombic crystal cell. The propagation vector is $k_1 = [0\ 0\ 1/3]$. At 74 K, the magnetic order becomes "anti-C" with a propagation vector $k_2 = [1\ 0\ 0]$. A third change in the magnetic order occurs at 40 K, and the new magnetic structure is essentially the "anti-C" structure but with the addition of a tripled magnetic component corresponding to a propagation vector $k_3 = [1/3\ 0\ 0]$.

Nanostructured Materials for Thermoelectric Energy Conversion

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Students:	5 Postdoctoral Fellow(s), 3 Graduate(s), 0 Undergraduate(s)
Funding:	\$1,406,000 (2014)

PROGRAM SCOPE

Investigation of the basic science of thermoelectricity and phonon transport, entailing the design of new nanostructured materials in order to gain fundamental understanding of how thermopower, electrical conductivity, and thermal conductivity can be manipulated independently so that the thermoelectric figure of merit can be improved. This program investigates several classes of novel materials ranging

from polymer hybrids to oxides, coupled with a strong theoretical component to guide understanding of the fundamental limits of these properties.

FY 2014 HIGHLIGHTS

In this period we have significantly advanced our understanding and control of transport in inorganic-organic hybrid materials. We have demonstrated a fundamentally new methodology to atomically resurface Te nanowires and band convert them from p-type to n-type materials, enabling integration into monomaterial modules. We have furthered our understanding of heat transport in silicon nanostructures by showing, for the first time, ballistic phonon transport in holy silicon nanostructures and providing new understanding of the dimensional criteria for crossover from ballistic to diffusive transport. Moreover, in superlattices, we directly observed the crossover from quantum mechanically coherent phonon transport to incoherent diffusive transport in superlattice materials. In the final period, we will further the coherent phonon work, extending it to silicon nanostructures as well. And we will also advance the promising work in band-conversion nanomaterials for thermoelectrics, pursuing the inverse behavior of n-type to p-type control. Controlling this class of physics in nanomaterials provides a fundamentally new handle to enhance the scalability and performance of nanoscale thermoelectrics.

Metamaterials

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Funding: \$398,000 (2014)

PROGRAM SCOPE

Many of the technologies that underpin our economy and enable our standard of living depend on advanced materials. Therefore, the engine for progress in many scientific disciplines is the discovery and understanding of new materials. Metamaterials are novel artificial materials that enable the realization of innovative properties unattainable in naturally existing materials. This research project will explore the theoretical understanding, analysis, development, fabrication, and experimental characterization of metamaterials, and investigate their feasibility for applications. In view of the complexity of electromagnetic interactions in metamaterials, state-of-the-art computational techniques to understand these materials, and collaboration with experimentalists to fabricate and characterize them, are essential. Finding and understanding mechanisms that minimize loss and increasing the operating frequency will be critical for future applications, such as solar energy harvesting and biomedical/terahertz imaging. We will develop new 3D nanofabrication techniques such as direct laser writing and experimentally realize dynamic and tunable metamaterials employing nonlinear and gain materials. Finally, we will characterize the physical properties of metamaterials and develop unique optical characterization techniques.

FY 2014 HIGHLIGHTS

We experimentally demonstrated broadband THz generation from resonant metallic metamaterials. A 40nm thin resonant metasurface can generate a non-linear response and THz generation efficiency that rivals millimeter thick standard non-linear crystals while completely eliminating the phase-matching problem. We developed patentable metamaterials for dispersion management, combining slow light and low absorption in matched, asymmetrically coupled interacting resonator metamaterials. This allows for tunable and very compact dispersion compensation devices to be developed, e.g. for use in fiber optical communication. We simulated and experimentally demonstrated diffractive photo-imprint materials on GaAs surfaces, which can be used for spatial and temporal THz pulse modulation. We analyzed the achievable surface conductivities in photo-excited GaAs surfaces and showed that they can be as good or better conductors than graphene while being similarly tunable. Moreover, we investigated the suitability of graphene for THz application. Because in current literature there is a significant gap between theoretical assumptions and experimental data on graphene, we demonstrate a simple set of figures of merit to compare graphene performance and direct optimization. We developed a new approach to low-loss resonators for metamaterials that does not suffer from the high dissipative losses metals encounter at optical frequencies. This concept is based on dark resonant bound states in dielectric structures or inclusions that are coupled to the propagating electromagnetic field by small, nonresonant metallic or dielectric scatterers. Finally, resonant magnetic permeability and negative index of refraction, n , from a single metallic film patterned as the Babinet complement of an electric quadrupole resonance was demonstrated numerically and the designs will be used to fabricate $n < 0$ at GHz and THz.

Synthesis and Characterization of Nanomaterial Heterostructures and Assemblies

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Funding: \$729,000 (2014)

PROGRAM SCOPE

The ability to synthesize, functionalize, and purify nanomaterials and to understand their transport, optical and mechanical properties lies at the forefront of current materials science research. As shown in the DOE report on Basic Research Needs for Solar Energy Utilization, nanostructured materials offer several potential advantages for solar energy conversion by providing relatively high electron and hole transport efficiencies, excitation multiplication possibilities, high surface-to-volume ratios, and short electron-hole diffusion lengths to junctions. However, the role of nanoscale heterojunctions in promoting exciton dissociation and charge separation is not understood. It is expected that junctions between low dimensional materials will behave differently as compared with bulk junctions. We will address the important question of the efficiency of charge separation versus recombination or trapping in a prototype heterogeneous nanomaterial systems: 0d-1d nanomaterial hybrids. We also expect to

develop a fundamental emphasis on synthesizing and understanding more complex nanoscale materials, including metallic heterostructures, of significance to the solar initiative. We have the ability to synthesize high quality samples and to study the properties and structure (both electronic and physical) of individual nanomaterial samples, thus eliminating the uncertainties in ensemble averaging over many structures. Working with our theoretical collaborators, these studies will clarify the potential of nanoscale heterojunctions for charge separation in solar electric generation.

FY 2014 HIGHLIGHTS

(1) We have synthesized and structurally characterized novel semiconducting nanoscale composite heterostructures composed of zero-dimensional (0D) CdSe nanocrystals coupled with both one- and three-dimensional (1D and 3D) rare earth metal-doped lanthanum metal phosphate materials. Subsequent optical characterization has demonstrated a clear dependence of the intrinsic charge and energy transfer processes in these systems on both (i) morphology and (ii) the presence of dopants. Our results show that our 1D and 3D heterostructures evince both photoluminescent (PL) quenching and a shorter average lifetime of CdSe quantum dots (QDs) as compared with unbound CdSe QDs. Optical heterostructure data are explained in terms of the energy level alignments of the constituent QDs and phosphates. *RSC Advances*, v.4, 34963 (2014). (2) Double-walled carbon nanotube (DWNT) - CdSe heterostructures with the individual nanoscale building blocks linked together by 4-aminothiophenol (4-ATP) have been successfully synthesized using two different and complementary routes, i.e. covalent attachment and pi-pi stacking. In general, heterostructures generated by non-covalent pi-pi stacking interactions evinced not only higher QD coverage density but also possibly more efficient charge transfer behavior as compared with their counterparts produced using covalent linker-mediated protocols. *Dalton Transactions*, v.43, 7480 (2014). (3) We have reported on the synthesis, structural characterization, and intrinsic charge transfer processes associated with novel luminescent 0-D CdSe nanocrystal – 1-D cerium phosphate: Tb nanowire composite heterostructures. Our composite heterostructures evinced both PL quenching and a shorter average lifetime as compared with unbound CdSe QDs and cerium phosphate: Tb nanowires. We propose that a photo-induced 0D-1D charge transfer process between CdSe and cerium phosphate: Tb accounts for the observed PL quenching and shorter lifetimes. *J. Phys. Chem. C*, v.118, 5671 (2014).

Sub-Wavelength Metamaterial Physics and Applications

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Funding: \$630,000 (2014)

PROGRAM SCOPE

This program explores a new class of photonic materials, metamaterials, by designing artificial atoms and molecules and their interactions. Our research investigates the novel physics of metamaterials to uncover unprecedented materials properties beyond that of natural materials.

FY 2014 HIGHLIGHTS

We have studied the unusual optoelectronic properties of single atomic layers of transition metal dichalcogenide (TMDC) materials, the two-dimensional semiconductors that hold great promise for nanoelectronic and photonic applications. Using two-photon excitation spectroscopy, we probed monolayers of tungsten disulfide, one of the most promising of 2D materials, and found evidence for the existence of excitonic dark states - energy states in which single photons can be neither absorbed nor emitted. These excitons were predicted from *ab initio* calculations to have an unusual energy sequence, plus excitonic binding energy and bandgaps that are far larger than was previously suspected for 2D TMDC materials. The discovery of very large excitonic binding energy and bandgaps and its nonhydrogenic nature in 2D semiconductor materials is important not only for understanding the unprecedented light-matter interaction arising from strong many-body effect, but also for electronic and optoelectronic applications, such as ultra-compact LEDs, sensors and transistors.

Elucidation of Hydride Interaction Mechanisms with Carbon Nanostructures and the Formation of Novel Nanocomposites

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Funding: \$642,000 (2014)

PROGRAM SCOPE

This program continues to support the Office of Basic Energy Sciences (BES) mission through the development of a basic understanding of the formation and the physicochemical properties of carbon nanostructures, formed by the interaction of doped carbon nanomaterials with hydrides and/or hydrogen gas. For many years extensive work has been conducted on hydrogen interaction with metals and alloys forming hydrides. The research work on metal hydrides involved significant number of studies and characterization efforts, where chemical, electronic, optical and magnetic properties were determined. Our work continues to focus on the unique class of materials, metal-doped carbon nanostructure and their interaction with hydrogen. Our work will continue to focus on understanding the formation of these materials and on investigating their chemical, electronic, optical and magnetic properties when reacted with hydrogen. Previous work in our group through BES programs has led to advances in control over a material's properties at the electronic, molecular, and atomic level, which serve as the foundation of new energy technologies and can support other aspects of DOE missions. Our group has observed related properties in the materials such as hydrogen storage and luminescence with potential applications in clean energy and energy storage. However, developing customizable functional materials requires relating the microstructure of the materials to their physical properties. Our research activities will be aimed at developing and characterizing a novel class of hydride materials based on metal-carbon nanostructures. The current work will investigate different carbon materials utilizing their structure as building blocks for achieving unique properties based on zero, one and two dimension (0D, 1D, 2D) structures such as fullerenes, carbon nanotubes and graphene respectively.

FY 2014 HIGHLIGHTS

Theoretical calculations (Prof. Jena, VCU) reveal that a new class of highly electronegative species can be created when a central metal atom is surrounded by superhalogen moieties. Building on this knowledge we were able to synthesize and characterize a stable hyperhalogen salt, $K[Al(BH_4)_4]$, whose anion, $Al(BH_4)_4^-$, has an extremely high electron affinity. Unlike the few hypersalts synthesized so far, this new salt is stable at temperatures of up to 154°C. Besides providing a new functional material, the work validates the use of computational studies for rational design of new compounds based on superhalogens and hyperhalogens. Building on our previous study of ionic mobility in a $LiBH_4-C_{60}$ system, a series of electrochemical measurements were performed to quantify the lithium ionic mobility in the material under various conditions. This study also demonstrated that the material can be used as a solid electrolyte in an all solid-state lithium ion battery. Theoretical calculations by Prof. Jena's group indicated that the $Li+BH_4^-$ bonding is perturbed in the presence of C_{60} resulting in a highly mobile Li ion due to the $C_{60}-BH_4^-$ interaction. This suggests a nanoionic mechanism is responsible for the enhanced Li ion mobility due to the formation of new interfaces at the nanoscale favoring the production of charge carriers. Further Laser-Desorption/Ionization Time-of-Flight Mass Spectrometry (LDI-TOF-MS) analysis of a sodium intercalated fullerene (Na_xC_{60}) in the hydrogenated state provided the first spectroscopic evidence for the formation of $C_{60}H_{60}$ among other highly hydrogenated fullerenes ($C_{60}H_{>36}$). This finding was also confirmed through deuteration of the same material to form $C_{60}D_{60}$. Current efforts in this system are focusing on the isolation of the $C_{60}H_{60}$ from the other fullerenes for further analysis and characterization. Our current work is aimed at understanding how hydrogen interaction with C_{60} and other carbon nanomaterials can potentially lend itself to other energy storage systems and energy conversion devices.

Synthesis and Processing Science

Institutions Receiving Grants

EARLY CAREER: Templated Bottom-Up Synthesis of Semiconducting and Nanostructured Graphene Materials

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Funding: \$150,000 (2014)

PROGRAM SCOPE

The objective of this project is to develop a fundamental understanding of how nanostructured graphene materials can be rationally synthesized from the bottom-up with atomic precision and exceptional properties. The research will focus on studying the nucleation and kinetics of graphene growth during chemical vapor deposition (CVD) on catalyst substrates in confined patterns and channels, controlling the crystallinity of the graphene materials, and learning the mechanisms that determine atomic ordering at their edges. The understanding that is gained will result in novel high-performance materials that could impact a number of energy technologies of national importance including low-energy semiconductor electronics, the efficient generation of electricity from solar and infrared light, and the high-density storage of energy in batteries.

FY 2014 HIGHLIGHTS

(1) We succeeded in understanding the effects of catalyst crystallography, precursor flux, and growth rate on graphene CVD at low temperature (T). Understanding growth at low T is important for improving the fidelity of nanostructured graphene that is grown via the process of barrier-guided CVD that we developed and studied in previous support periods. We learned that graphene is grown more efficiently on Cu(111) than on other low-index Cu facets. Through control over the precursor flux and growth rate, we successfully synthesized continuous, high-quality monolayer graphene films at 750 °C, which is 125 °C lower than previous reports using CH₄ as a precursor and Cu as the catalyst and ~250 to 325 °C lower than the typical T used in literature to grow graphene via CVD. (2) We studied and developed a novel method to thermally anneal out etch-induced disorder from the edges of top-down patterned graphene nanostructures. In FY 2013, we identified a hydrogen concentration dependent critical methane concentration (CMC) in which the net growth rate of graphene during atmospheric pressure graphene CVD on Cu is zero, which occurs when intermediate CH hydrocarbons attach to graphene edges at the same rate as graphene etches. In FY 2014, we succeeded in converting disordered edges of graphene nanostructures into relatively smooth zigzag edges via annealing on a Cu(111) substrate at the CMC. This work is important because now graphene nanostructures with smooth zigzag edges can be achieved using any conventional top-down subtractive lithography. (3) In preliminary data, we have discovered how to directly grow graphene nanoribbons that are extremely narrow (< 10 nm) and that have smooth armchair edges, directly by CVD. Remarkably, the ribbons are self-defining and grow from the bottom-

up without any lithographic template, and they align themselves. This is a breakthrough in nanoribbon synthesis that will be studied further in FY 2015.

Studies of Surface Reaction and Nucleation Mechanisms in Atomic Layer Deposition

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Funding: \$200,000 (2014)

PROGRAM SCOPE

Atomic layer deposition (ALD) is a method for depositing thin films of numerous semiconducting, insulating and metallic materials using an alternating series of self-limiting reactions between gas phase precursors and the substrate. ALD is proving to be an enabling technique for creating the innovative nanostructured materials needed for future applications, including those in solar energy and photoelectrocatalysis. The aim of this project is to perform both experimental and theoretical studies to uncover surface reaction and nucleation mechanisms active during ALD. A combination of *in situ*, *ex situ*, and *in vacuo* X-ray photoelectron spectroscopy, infrared spectroscopy, synchrotron radiation photoelectron spectroscopy, and synchrotron radiation X-ray diffraction studies are employed, together with complementary density functional theory calculations and nucleation modeling. The research focuses on representative ALD systems for the deposition of two categories of material: binary and ternary metal oxides, such as zinc tin oxide, and noble metals, such as Pt and Ru. These materials are chosen not only for their technological importance to the energy area, including their useful optoelectronic or catalytic properties, but also because they serve as prototypical systems that allow exploration into fundamental question about ALD. The mechanistic details obtained from these studies can be used to guide and inform future precursor and process development. The work is expected to lead to new insights into ALD processes. Overall, the main objectives of this study are to develop an improved understanding of the chemical reactions driving both nucleation and steady state growth in ALD, and to provide the scientific foundation required for the ultimate design and synthesis of new materials for applications in energy, electronics, and catalysis.

FY 2014 HIGHLIGHTS

We carried out studies to advance the understanding of surface reaction and nucleation mechanisms in atomic layer deposition (ALD) with a focus on two important categories of ALD materials: metals and metal oxides. We completed and tested a portable reactor for *in situ* ALD studies. The chamber design allows it to be incorporated within a rotating diffractometer and permits use for both x-ray scattering and diffraction studies. In metal ALD, we investigated nucleation during Pt ALD on graphene. We demonstrated selective ALD of Pt at the line defects of graphene, notably grain boundaries, due to the enhanced chemical reactivity of these defects. We investigated the effect of a more reactive counter reactant, i.e. ozone, on nucleation and growth during Pt ALD on silicon dioxide. The growth rate using ozone is higher than that using either air or oxygen counter reactants. We performed *in situ* and *ex situ* thin film diffraction and scattering studies of Pt ALD at the Stanford Synchrotron Radiation Lightsource (SSRL). We tracked Pt ALD growth from initial island nucleation, to island growth, coalescence, and film formation. We showed that the in-plane strain of the Pt lattice changes from compressive strain to

tensile strain when the individual islands coalesce into a continuous film. The growth of zinc tin oxide (ZTO) was studied as a model system for ALD of ternary metal oxides, using alternating growth of tin oxide and zinc oxide. We showed that the ZTO growth rate is strongly reduced as compared to the growth rates of the binaries, due to a significant reduction in surface reaction site density during the tin oxide cycle, which may be a consequence of the different numbers of ligands on the two precursors. The correlation between precursor molecular structure and material growth that we established for the ZTO system will likely apply to other ALD processes as well.

Molecule-Sorbent Interactions in Metal Organic Framework Materials

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Funding: \$360,000 (2014)

PROGRAM SCOPE

The aim of this program is to develop a fundamental mechanistic understanding of the interaction of small molecules— H₂, N₂, O₂, CO₂, H₂O, NH₃, SO₂, NO, NO₂, CH₄ and C_xH_y—in porous metal organic framework (MOF) materials, using a combination of novel synthesis, theoretical analysis, and characterization. In particular, we combine high-pressure/low-temperature infrared (IR) absorption and Raman measurements, adsorption isotherms and isosteric heat of adsorption measurements with first-principles calculations based on van der Waals density functional (vdW-DF) modeling, to study the behavior of a number of molecules in different MOF materials. One of the goals is to provide insight concerning the role of unsaturated metal centers or active sites grafted to combine with especially designed ligands to enhancing molecular uptake, selective adsorption, and diffusion. The short term impact of our work will result from the control and the understanding of common MOF systems, making it possible to determine the theoretical loading limits and stability of a specific class of materials, and the diffusion and the co-adsorption interactions of a variety of gases and gas mixtures. The long term impact will involve the development of 1) theoretical and experimental methods to gain a fundamental understanding of molecular interactions within these systems, and 2) new classes of microporous MOFs with enhanced molecular binding, selectivity, and diffusion properties.

FY 2014 HIGHLIGHTS

Water adsorption was shown to be reversible in MOF-74 below the water condensation pressure at room temperature. At ~150 °C, a reaction takes place even at low water vapor pressures. This finding provides insight into the long-lasting question of MOF-74 degradation and adds to the understanding of molecular water interaction with cation-exposed surfaces to enable development of more efficient catalysts for water dissociation. By examining the competitive co-adsorption of several small molecules in M-MOF-74, we find that the binding energy at the most favorable (metal) site is not a sufficient indicator for prediction of molecular adsorption and stability in MOFs. Instead, the occupation of the open metal sites is governed by kinetics, whereby the interaction of the guest molecules with the MOF organic linkers controls the reaction barrier for molecular exchange. A new Co-MOF was shown to be capable of effective capture and separation of xenon from other noble gases, as a first example of

commensurate adsorption of atomic gases near ambient conditions. We have also developed new luminescent MOFs (LMOFs) that show fast and effective detection of high explosives such as 1,3,5-Trinitroperhydro-1,3,5-triazine (RDX). The effect of porosity and electronic structure of the LMOFs on their sensing performance was evaluated, and the importance of both electron and energy transfer processes on the fluorescence response elucidated. In addition, we investigated a water stable zirconium-porphyrin MOF as acid sensor that exhibits distinct and reversible colorimetric and fluorescent 'turn-off-turn-on' pH response. Computationally screening MOF-74 structures with 25 different metals for their adsorption properties, we found a series of possible MOFs that bind CO₂ stronger than H₂O and thus are excellent candidates for novel carbon-capturing applications.

Metal Oxide Core Shell Nanostructures as Building Blocks for Efficient Light Emission

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

The goal of this research is to synthesize core-shell nano-structured metal oxide materials and investigate their structural, electronic and optical properties to understand the microscopic pathways governing the energy conversion process, thereby controlling and improving its efficiency. To rationally design such a core-shell nano-structured metal oxide material with larger absorption cross-sections, this work tackles two critical aspects of the materials engineering: (1) elucidate the growth mechanism of these nanostructured materials and its effect on the resulting photo-efficiency and (2) control the spatial distribution of optically active rare-earth (RE) ions by atomic layer deposition, since the location and spatial distribution of the rare-earth-ions as well as the microstructure and morphology are critical to the optical performance of these materials at reduced dimension and dimensionality. Specifically, this program focuses on: a) developing a hydrothermal process to synthesize the nanometered core and a radical enhanced atomic layer deposition process to control the distribution and activity of the dopant ions in the shell, b) monitoring the formation of metal hydroxides and metal oxide nanostructures by synchrotron radiation based x-ray absorption and diffraction analyses, c) identifying the chemical coordination of the rare-earth ions in the host and quantifying the concentration of optically active rare-earth ions, d) measuring the photoluminescence of these nanostructures and determining the absorption cross section for rare-earth ions and its dependencies on the doping concentration and the host composition, and e) integrating these synthesized one-dimensional rare-earth doped materials into simple devices to test their optical performance. This research provides optimized processes for synthesizing complex rare-earth ion doped metal oxide nanostructures and thin films, and lay the foundation of future generations of optical devices.

FY 2014 HIGHLIGHTS

Core-shell nano-structured metal oxide materials were synthesized and investigated for their structural, electronic and optical properties. The growth mechanism of the RE-oxide nanostructure cores during hydrothermal processing was delineated by synchrotron radiation based x-ray absorption and diffraction analyses. The shell was synthesized primarily by sol-gel processing and more recently by atomic layer

deposition and it reduced the effect of the surface quenching sites by increasing the distance between active ions and the surface hydroxyl groups. The luminescent fingerprint can be controlled with proper doping in the shell structure and a precision control of the dopant distribution. A theoretical comparison between the optical Judd-Ofelt analysis and the modeled extended X-ray absorption fine structure (EXAFS) spectroscopy was used to understand the effects of the dopant concentration and particle architecture on the luminescence parameters. By spatially controlling the RE dopant within a core-shell nanostructure, it is possible to increase the luminescence intensity and emission lifetimes. Furthermore, the effect of luminescence sensitization with the addition of Yb^{3+} was studied based on the upconversion luminescence dynamics and emission spectrum indicating a competing depopulation mechanism for the $^4I_{11/2}$ energy level. Finally, an efficient and high quality $\text{RE}^{3+}:\text{LaPO}_4$ white light phosphor was designed with specific criteria based on the energy dynamics elucidated from the study of $\text{Er}^{3+}:\text{Y}_2\text{O}_3$ nanoparticles. Simulation work is under way to study the resonant energy transfer (RET) in closely packed optically active rare earth ion core-shell systems exhibiting discrete and inhomogeneous ion distributions and to assess their potential impact of rapidly developing processing technology. Specifically, the effects of RE ion identity and proximity on the photoluminescence (PL) are investigated for various metal oxide hosts.

A Unified Understanding of Residual Stress in Thin Films: Kinetic Models, Experiments and Simulations

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Funding: \$145,000 (2014)

PROGRAM SCOPE

The goal of our research is to develop a quantitative understanding of residual stress in polycrystalline films in terms of the underlying fundamental kinetic processes and microstructural parameters. Thin films are critical to many advanced technologies, but the residual stress can severely limit their performance or induce failure. The stress is measured in real-time while the film is growing using a wafer curvature technique. We are developing models to relate the measured stress to the underlying physical processes under different conditions. Our approach is to describe the stress at the point where different grains within the film meet (called the triple junction) as the film grows. The resulting stress is explained in terms of balance between attractive forces between the grains and insertion of atoms from the surface into the boundary between grains. It explains the dependence on the growth rate, microstructure and material parameters as well as the dependence on the surface morphology as the film evolves from isolated islands to a flat film. To explore and refine this model, we perform carefully-designed experiments to quantify the relationship between the processing conditions, microstructure and resulting stress. We use the growth of lithographically-patterned films to create islands of a well-controlled geometry that enables us to know precisely the evolution of the surface morphology during film growth. In unpatterned films, we characterize the resulting microstructure using cross-section electron microscopy in order to understand the dependence of the stress on the growth rate and grain size. From these results we are building an understanding of stress evolution in multiple material systems. The eventual product of this work will be to predict the stress in single component and alloy thin films in terms of the processing conditions and materials parameters.

FY 2014 HIGHLIGHTS

In the past year, we have made significant progress in two related series of studies. In the first, we studied stress in films grown on patterned substrates so that the morphology during growth could be known. These studies were performed on both 1-dimensional and 2-dimensional patterned arrays in which the islands grew as half-cylinders and half-spheres, respectively. The difference between the two patterns enabled us to study how the different geometries during island coalescence affect the resulting stress, as well as study the effects of anisotropy in the island array. The results were interpreted in terms of a model that we developed that considers the stress that develops at the boundary between the islands. The island geometry and film growth rate both affect the evolution of the boundary, as predicted by the model. The model was able to explain the results for both types of island arrays for multiple growth rates. For the 1-d array, we were also able to study the effect of the pattern spacing on the stress. The good agreement supports the validity of our model for explaining residual stress. In the second set of studies, we performed systematic experiments to explore the relationship between the stress evolution, the grain size and the growth rate in unpatterned films. We did this by measuring the stress as we grew the film for multiple growth rates. Afterwards, we characterized the grain size by cross-sectional electron microscopy measurements. By knowing the growth rates at different times, we could correlate the grain size at different thickness with the growth rate and resulting stress. These are the first data that clearly separate the effects of growth rate and grain size on stress. Previous studies have not considered how they are inter-related.

Electric-Loading Enhanced Kinetics in Oxide Ceramics: Pore Migration, Sintering and Grain Growth

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Funding: \$600,000 (2014-2017)

PROGRAM SCOPE

The project has reported several novel observations of electric-loading effects on sintering, grain growth and pore/bubble migration in cubic yttria-stabilized zirconia (YSZ) ceramics. Two fundamental atomistic mechanisms, one controlled by surface diffusion of cations, the other caused by supersaturation of oxygen vacancies, have been identified. They led to sintering, without grain growth, of YSZ at unprecedentedly low temperature, and to 10000 times faster microstructure evolutions that can be controlled by electric polarization. These findings may be applied to aid processing of YSZ and other ceramics, as well as assessing the stability and reliability of high temperature energy devices. To further basic understanding of atomic defects and microstructures, the project extends the above research to single crystal studies, electrochemical studies, *in situ* TEM studies, and continuum and computational modeling. Specific topics investigated include: electro-migration of pores/bubbles and second phase particles in YSZ single crystals, measurement of internal electric and oxygen potentials in YSZ electrolyte, field-enhanced grain growth in particle-containing YSZ, *in situ* imaging of bubble migration in YSZ under an electric or oxygen potential bias, boundary value problems of electro-migration, and simulations of defect configurations, energetics and dynamics. By strategic exploration of novel phenomena in phase/microstructure stability and defect kinetics engendered by electric loading on cubic YSZ, this study will expand the potential scope of utilizing electric effects for ceramic synthesis and processing.

More broadly, the fundamental thermodynamic and kinetic information gained from the research will significantly advance our scientific knowledge of a class of oxide ceramics that find myriad energy applications from oxide electrochemical cells, thermal barrier coating, to nuclear fuels and waste storage.

FY 2014 HIGHLIGHTS

We have succeeded in demonstrating electro-migration of dispersed particles of alumina, an oxide second phase, in YSZ ceramics, for the first time. Using two-step sintering, we also obtained dense bulk YSZ ceramics of an unprecedentedly small grain size. We further discovered in such ceramics grain growth kinetics that contradicts the conventional kinetics of exhaustion, such as Hillert's parabolic law. Instead, the grain size initially follows an exponential law, which has never been reported before. These results provide new opportunities to fundamentally understand the kinetic and thermodynamic aspects of defects and structure in this class of technologically important ceramics.

High-Throughput Preparation and Characterization of Vapor-deposited Organic Glasses

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Funding: \$170,000 (2014)

PROGRAM SCOPE

Glasses combine the disordered structure of liquids with the mechanical properties of solids. On macroscopic scales, glasses can be extremely homogeneous, and their properties can be tuned continuously through composition and processing conditions. These are important factors explaining the significant role of glassy materials in developing technologies including organic electronics. In this project, we are working to expand considerably the range over which the properties of organic glasses can be tuned by making use of recent developments in physical vapor deposition (PVD). It has recently been established that PVD can prepare glasses that have much higher density and kinetic stability than can be attained with other methods and that such glasses can exhibit anisotropic packing. We are developing a temperature-gradient stage to prepare a wide variety of highly stable glasses in a single deposition. We perform ellipsometry and wide angle X-ray scattering at ~40 positions along the temperature-gradient. In this way, we efficiently characterize how a 130 K range of substrate temperatures influences the density, anisotropy, and molecular packing of vapor-deposited glasses. We are performing these measurements on glasses made of four molecules, including a model glassformer and three molecules important in organic light emitting devices (OLEDs). The OLED molecules were chosen to explore the effect of molecular shape on the properties of PVD glasses and to understand the potential role of highly stable glasses in these technologies. In particular, the anisotropy of PVD glasses may be advantageous for some applications and it appears that varying the substrate temperature allows access to a wide variety of anisotropic packing arrangements while maintaining high density and high kinetic stability.

FY 2014 HIGHLIGHTS

We have studied glasses of three molecules that have been used to make organic light emitting diodes (OLEDs). We used physical vapor deposition onto a silicon wafer with a 130 K temperature gradient so as to efficiently prepare a wide range of glasses of each compound in a single deposition. All these glasses were then interrogated individually using spectroscopic ellipsometry. Our results for these three molecules show a remarkable dependence of molecular orientation upon substrate temperature and this dependence is qualitatively similar for the three molecules. At the lowest substrate temperature, all three molecules lie down such that their long axes are almost completely in the plane of the substrate; this arrangement is known to be advantageous for emitters in OLEDs as it can increase device efficiency by a factor of 1.5. At a higher substrate temperature, all three molecules show a tendency to stand up such that their long axes are normal to the plane of the substrate. Our high-throughput methodology allows us to differentiate between the effects of molecular shape and substrate temperature for the first time. We find substrate temperature to be the dominant control variable and this suggests that a wide range of molecular orientations might be achieved via physical vapor deposition with almost any organic molecule; this provides a new dimension for optimizing the properties of OLEDs and other organic electronics devices. Computer simulations allow an interpretation of these results in terms of the molecular orientation present at the surface of the equilibrium liquid and allow optimism that molecular orientation in vapor-deposited glasses might ultimately be predicted from computer simulations.

Atomic Layer Controlled Growth of Artificially Engineered Pnictide Superlattices By Design

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Jointly funded by "Experimental Condensed Matter Physics" and "Synthesis and Processing Science"

PROGRAM SCOPE

Since the discovery of superconductivity in iron-based materials significant progress has been made in the fabrication of high quality bulk and epitaxial thin film materials to explore their intrinsic properties and evaluate novel device applications. The superconducting mechanism, structural transitions, magnetic behavior above and below T_c , interfacial phenomena, and critical current and flux-pinning behavior have all been recognized as critical to progress toward understanding the pnictides. Artificial layered pnictide superlattices with atomically sharp heterointerfaces offer unique opportunity towards tailoring superconducting properties and understanding the mechanisms of superconductivity by creating model structures which do not exist in nature. Our main tasks are to create and control pnictide superlattices and heterointerfaces at the atomic level, to understand the relation between structure, magnetism and superconducting properties, and to design and grow novel pnictide superlattices tuned to take advantage of the superconducting structure/property relationships possible in this unique new superconductor. The thrusts of our proposed work are: (1) Atomic-layer-controlled growth of artificially engineered superlattices. (2) Designing interfacial superconductivity at pnictide and FeSe interfaces. (3) Investigation of interaction between superconductivity and magnetism by proximity effect (4) Understanding and control of flux-pinning mechanisms (5) Study of growth mechanisms of

heteroepitaxial superlattices and artificial pinning centers. The proposed work investigates the basic physical processes of novel superconductivity, primarily by looking at its interaction with magnetism on a microscopic scale, and the role these play in the flux pinning process. We also extend these fundamental investigations to explore routes to interfacial superconductivity in these systems.

FY 2014 HIGHLIGHTS

We investigated the superconducting properties of single- and multilayer Co-doped BaFe₂As₂ (Co-Ba122) thin films grown on CaF₂ and (LaAlO₃)_{0.3}(Sr₂AlTaO₃)_{0.7} (LSAT) substrates. We confirmed the significant improvement of the critical temperature in the film on CaF₂ and we demonstrated that the multilayer deposition has no detrimental effect on T_c. We found that deposition on CaF₂ produces much cleaner films compared to films on LSAT, since on CaF₂ the substrate absorbs oxygen preventing the formation of the high density of defects present in the LSAT case. The result of this oxygen reaction is that in the single layer on CaF₂ (CaF-S) the only visible defects are dislocations. Moreover, the different trend of angular dependence of critical current density in CaF-S at intermediate temperature suggests an increasing contribution of point defects with decreasing temperature. The multilayer film on CaF₂ (CaF-M), grown with insertion layers enriched in BaO, does have defects including short nanorods, round particles and flat particles similar in size but with a lower density to those in films on LSAT. Despite the different pinning mechanisms that affect the shape of the angular dependence of J_c, the single layers on both substrates roughly have similar J_c at the same reduced temperature. In contrast the multilayer deposition on CaF₂ is 2-3 times more effective in increasing J_c with respect to the corresponding single layer than in the LSAT case. This results in a record high pinning force (F_p) of 84 and 70 GN/m³ in Ba122 phases (H//ab and H//c, respectively), significantly larger than reported previous values in the Co-Ba122 phase and higher-T_c P-Ba122 phase. Applications interest is strengthened by their notably better in-field performance than in Nb₃Sn.

Using Energetic Gas Jets to Enable New Modes of Focused Electron Beam Induced Deposition

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Funding: \$220,000 (2014)

PROGRAM SCOPE

Focused Electron Beam Induced Deposition (FEBID) is an emerging method of directly fabricating three-dimensional nanostructures from a variety of materials. There exists a wide range of potential applications for FEBID, since it is of a relatively low cost, inflicts minimal surface damage, and can achieve high feature resolution as compared to other deposition systems. However, the FEBID penetration as a manufacturing tool remains limited due to low deposition rates, poor deposit purity, and a trade-off between an achievable deposition rate and deposit resolution. A great deal of fundamental science relevant to gas jet assisted EBID is not well understood, such as predicting the adsorption probability of impinging molecules onto the surface and the dissociation probability of adsorbed molecules due to secondary electrons. Gas injection as a method of precursor delivery presents unique opportunities to enhance FEBID performance. In particular, use of energetic jets allows modulation of the local effective surface temperature of the substrate and control precursor sticking to

the surface. We have demonstrated that the energy of an inert gas jet impinging upon the surface is sufficient to raise the effective temperature of the surface, to greatly enhance the pre-adsorbed precursor diffusion rate and, in turn, to significantly improve the deposit growth rate. We propose experiments and simulations that would allow us to develop the first principle sticking probability model(s) for gas-jet FEBID, thus enabling development of comprehensive system design tools. This research will provide a significant benefit to society by developing a nanomanufacturing tool for making topologically complex semiconductor nanostructures and devices. Potentially transformational benefits are expected, impacting a wide range of applications including energy conversion, optoelectronic communication, and 3D nano-electro-mechanical devices for separation and sensing.

FY 2014 HIGHLIGHTS

Complimentary experimental research and modeling have been performed to develop the first principle sticking probability model and relevant process simulations in order to enable comprehensive energetic gas-jet enhanced Focused Electron Beam Induced Deposition (FEBID) simulation tools with minimal empirical inputs. The thermal response of the substrate subjected to the energetic gas-jet impingement has been mapped using a micromachined array of resistor temperature detectors (RTDs), which is the first time such a spatially-resolved experimental data has been obtained in this research field. In concert with the experimental measurements of thermal effect of the gas jet, the comprehensive simulation framework for the gas-jet has been developed to accommodate – for the first time – continuum, transitional, and molecular flow regimes in a unified computational approach based on Direct Monte Carlo Simulations. We have shown that FEBID can be utilized to covalently functionalize graphene with high degrees of control, owing to its intrinsic patterning resolution down to a few nanometers. Controlled chemisorption of carbon atoms or hydrocarbon radicals using FEBID can be effective in modifying the electronic and magnetic properties of graphene. In particular, we assessed the nature of adsorption states of FEBID-produced carbon on graphene as function of the deposit location and suggested a laser-assisted post-deposition process to remove parasitic carbon deposits, using first-principles calculations and complementary Raman experiments. In combination with demonstrated post-deposition “cleaning” process using laser ablation to remove detrimental “halo” carbon deposits with graphene remaining intact, this approach establishes the FEBID as a novel tool for controlled covalent functionalization of graphene with applications to electronic device fabrication and sensing on nanoscale.

Forces, Crystallizations and Assembly in Nanoparticle Suspensions

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Funding:	\$250,000 (2014)

PROGRAM SCOPE

In this research, complementary theoretical and experimental methods are used to quantify the binding of structure-directing agents (SDAs) to coinage-metal surfaces and to resolve the mechanisms by which SDAs mediate shape-selective growth. On the theoretical side, first-principles, dispersion-corrected, density-functional theory (DFT) is used to quantify the binding of polymeric and small-molecule SDAs, as

well as solvent, to low Miller-index surfaces of the coinage metals. Force fields have been and are being fit to describe binding in these systems and tested against DFT and experiment. Large-scale molecular dynamics (MD) simulations are being conducted to understand the solution-phase growth and structural transformations of isotropic Ag nanoparticles, as well as structural transformations and aggregative, solution-phase growth mechanisms for coinage-metal nanowires and Ag nanosheets. Additionally, we continue to investigate the growth and assembly of titanium dioxide nanoparticles using empirical force fields. On the experimental side, two experimental platforms - isothermal titration calorimetry (ITC) and in-situ, liquid-phase, high resolution transmission electron microscopy - are being developed to understand the influence of SDAs on anisotropic seeded growth in coinage-metal colloidal syntheses. These studies are quantifying SDA binding energies to various nanostructures and provide a real-time, in-situ view of nanostructure growth.

FY 2014 HIGHLIGHTS

Theoretical studies focused on understanding oriented attachment (OA), where we applied a newly developed reactive force field to demonstrate how water mediates OA of anatase nanocrystals (Nano Lett. 14, 1836, 2014; Chem. Eng. Science 121, 10, 2015). A second thrust focused on understanding the workings of SDAs in the synthesis of noble-metal nanostructures. We developed an empirical force field to describe the interaction of polyvinylpyrrolidone (PVP), polyethylene oxide (PEO), and (poly)ethylene glycol with Ag surfaces (J. Phys. Chem. C 118, 3366, 2014). We wrote two invited reviews on the workings of PVP and PEO as SDAs for Ag nanostructure synthesis (Molecular Simulation 40, 134, 2014; J. Chem. Eng. Data 59, 3113, 2014). We used MD to calculate binding free energies of PVP analog molecules to Ag surfaces and compare the results to experiments (see below). We used MD to demonstrate that 5-fold-twinned noble-metal nanowires have a body-centered orthorhombic structure (J. Phys. Chem. C 118, 18746, 2014). We also completed a study of the binding of PVP to Au surfaces involving DFT and empirical force fields and a manuscript will be submitted on this work in early 2015. Studies with DFT and MD are demonstrating how hexadecylamine is an effective SDA for the formation of {100}-faceted Cu nanostructures. In an effort to quantify the thermodynamics of PVP adsorption to Ag nanostructures, a new method has been developed for conducting isothermal titration calorimetry (ITC) experiments. The details of this method have been submitted to the Journal of the American Chemical Society and a provisional patent has been filed. The advantages of the new method have been detailed in a publication recently submitted to Nature Methods, which demonstrates for the first time, the direct calorimetric measurement of a picomolar (pM) binding system. The new method has been used to analyze the binding energy of small molecules adsorption to Ag nanostructures and the nanoscale cation exchange of Ag with CdSe nanoparticles.

Kinetic and Mechanistic Study of Vapor-Phase Free Radical Polymerization onto Liquid Surfaces

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Funding: \$250,000 (2014-2015)

PROGRAM SCOPE

This proposal aims to experimentally and computationally study the fundamental aspects of a new and exciting technique to deposit polymer particles and films onto liquid surfaces via initiated chemical vapor deposition (iCVD). This is a novel technique pioneered by the PI which is expected to revolutionize materials development by offering new initial conditions for growth as well as additional degrees of freedom afforded by the unconstrained nature of the liquid surface. This technique could lead to a more cost effective, scalable process for fabricating thermally stable films for fuel cell applications as well as nanoparticles for a range of applications in solar cells, photonics, and computer memory devices. In addition, the ability to introduce patterns into the liquid surface, for example standing wave patterns and vortices, could allow for the shape of the resulting particles to be controlled. The molecular origins associated with polymerization on liquid surfaces will be determined by studying how the adsorption and arrangement of the monomer molecules on the surface of the liquid affects the polymer molecular weight and diffusion. In addition, multiscale simulations will be performed to determine the molecular mechanisms involved during polymerization on liquid surfaces. The results of this study will uncover fundamental aspects of the process-structure-property relationships that govern the deposition process. The field of vapor phase deposition of organic and inorganic materials onto liquids is evolving rapidly with a broad range of applications, and it is expected that the conclusions from this study will have broad relevance on the characterization and understanding of the liquid/vapor interface.

FY 2014 HIGHLIGHTS

We are currently investigating nanoparticle formation at the liquid surface as a function of several parameters including liquid viscosity and molecular weight. We are using dynamic light scattering and quartz crystal microbalance measurements to determine how surface tension, molecular weight, viscosity, and absorption affect the nanoparticle size distribution. In order to observe the particle growth directly on the liquid surface, we have developed a method in which the particles are deposited onto liquid poly(dimethyl siloxane) (PDMS) with cross-linker. The PDMS is then cured at room temperature and imaged. This new imaging technique allows us to determine the location of nanoparticle growth relative to the interface and provides us with new information about the spacing between particles on the interface.

New Frontiers in III-Nitride Selective Area Growth: Nanoepitaxy and Lateral Evolution

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PROGRAM SCOPE

Selective area growth (SAG) is a phenomenon in thin-film deposition where the sample surface is masked by a dielectric or refractory layer such that growth takes place only in exposed window regions. The selectivity is introduced due to large disparities in incorporation energetics and kinetics between the mask and window region. This proposal aims to bring the SAG of GaN to a new state of art, so as to unleash the full potential of this wide bandgap semiconductor family in photonics and microelectronics.

The concept of SAG will be extended to a mesoscopic scale and combined with sophisticated lithography and micromachining to create novel geometric configurations and conditions not attainable at present. A major objective is the universal, chip-level, and heterogeneous integration of GaN devices with other substrates and devices (such as CMOS electronics). We propose the application of the evolutionary selection process through confined SAG growth to create mono-crystalline GaN on oxide and other amorphous substrate. A textured nitride thin film, having preferred out-of-plane alignment, is first deposited and then lithographically patterned into the seed for the subsequent lateral overgrowth. The lateral growth in a constricted channel, which can be implemented as either an open groove or a closed tunnel, will induce a lateral orientation selection based on the competition of growth velocities among grains having different in-plane orientations. The consequence of this lateral competition selection is a great reduction in the angular dispersion of in-plane crystallographic alignment and the creation of monocrystalline GaN on arbitrarily-chosen templates.

FY 2014 HIGHLIGHTS

We have shown a full demonstration of the ability to grow GaN on an amorphous SiO₂ surface. Synchrotron micro-focused XRD analysis of evolutionary-section grown GaN on SiO₂ validates the intrinsically high microstructural quality of the GaN produced with this method, and shows its suitability for the production of high-performance GaN-based devices on amorphous surfaces. Analysis of channel confined growth for GaN on amorphous surfaces is expected to enable a scalable and effective method for integration of device quality semiconductor crystals with non-crystalline substrates, and further apply the use of channel confined masks to achieve other desirable growth configurations. And we carried out further investigation of confined lateral overgrowth of GaN tiles about the strain and microstructural properties, as well as the growth mechanism studying. The strain estimated from Raman results was found to be gradually reduced to zero from the center to the edge of tiles. Most of the dislocations in AlN are blocked by SiO₂ floor mask except the region of exposed AlN seed. Dislocations originated from the AlN seed region bend lateral into the GaN tiles. Therefore the density of vertical dislocations propagating into the top surface of GaN is reduced dramatically. The growth mechanism of confined lateral overgrowth (CLO) has been investigated by studying the growth behavior in the rectangular channels. The growth behavior was also simulated by COMSOL with concerning gas-phase diffusion. The experimental thickness profiles of GaN exhibited similar trends as the results from simulation, indicating that the growth behavior of CLO is dominated by gas-phase diffusion and can be predicted by the simulation.

Understanding and Controlling Nanoscale Crystal Growth Using Mechanical Forces

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Funding: \$450,000 (2014-2017)

PROGRAM SCOPE

Synthesis of high-quality 2D materials such as graphene requires control not only over the nucleation and growth of each crystal domain, but also over the interactions among populations of domains growing simultaneously. To enable future energy-efficient electronics, membranes, and other

applications of graphene, it is most desirable to produce graphene directly on a functional substrate. Current transfer methods from metallic growth substrates can degrade film quality and introduce harmful residues. In this program we will explore the mechanisms of graphene growth at the interface between a metal film and dielectric or semiconducting substrate (e.g., SiO₂, h-BN). By understanding of the role of film microstructure, mechanical stress, carbon diffusion and precipitation kinetics, and interface properties, we believe it will be possible to establish position-controlled nucleation and growth of interfacial graphene domains that combine into highly uniform graphene films. The program will leverage specialized techniques in our laboratory including *in situ* optical spectroscopy of the substrate along with rapid temperature control, and instruments that can apply and measure controlled stresses in thin films. The program will also extend our multi-scale understanding of nanoscale carbon precipitation and collective self-organization at the mesoscale, which was recently developed in the context of carbon nanotube growth. Overall, this research will establish interfacial growth as a means of fabricating high-quality graphene films directly on non-metal substrates, with potential relevance to other 2D crystal systems.

FY 2014 HIGHLIGHTS

The funding period began on 9/15/2014.

Laser Fabrication of Active Single-Crystal Architecture in Glass

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Funding: \$300,000 (2014-2015)

PROGRAM SCOPE

Numerous energy devices rely on the availability of suitable single crystals of complex compositions in appropriate form. The conventional thermal processes for fabricating single crystals from the melt are not suitable for many important multi-component systems because either the material decomposes before melting, or undesired phases form by incongruent solidification of the melt. We are addressing this generic challenge of material fabrication by a laser-crystallization process that bypasses melting, yet would allow the control of size, geometry and orientation of the single crystal. As a proof of concept our goal is to fabricate a bend in the single-crystal line and then a 2D planar single crystal, without altering the lattice orientation. Our approach is based on two hypotheses: (i) The crystal growth can be controlled using a dynamic temperature profile which determines rate-controlling local diffusivities and interfacial reaction kinetics. (ii) A laser can produce complex heating profiles that are not possible with any other technique. Consequently, we are determining the heat profile and the dependence of growth on local (anisotropic) temperature gradient. Then appropriate dynamic temperature profile is established to yield specified crystal geometry (shape and size) in a given glass. High resolution spatial light modulator technology, which has become readily available only recently, is to be used to shape precisely and vary dynamically essentially arbitrary beam profiles. The initial crystal growth experiments are to be performed on IR transmitting chalcogenide systems to yield active crystal phases with superior piezoelectric, photoelectric, pyroelectric and pyro-optic properties. The chosen systems allow a systematic variation of network dimensionality, hence growth anisotropy. Successful understanding of

single crystal growth process in these compositions would help establish its broad applicability to various other glass forming systems.

FY 2014 HIGHLIGHTS

We have demonstrated the first unequivocal fabrication of a laser-induced single crystal in a glass via solid \rightarrow solid transformation i.e. without melting. Specifically, Sb_2S_3 crystals are fabricated on the surface of Sb-S-I glass, where temperature and chemical gradients induce single crystal growth and suppress polycrystallinity. Here the nucleation rate in the supercooled liquid state is much slower than the crystal growth rate, which facilitates the formation of single crystal from a given nucleus as the laser is traversed above a threshold speed. Through the control and optimization of laser writing parameters, we have succeeded in forming straight and bent single-crystal lines, and then 'stitched' them to form a 2D single-crystal on the surface of glass. The lattice of the single-crystal line fabricated at or near the surface of Sb-S-I glass rotates gradually along its length. To elucidate the mechanism of this unexpected phenomenon, the crystals were analyzed by scanning X-ray micro-diffraction (microSXRD) at the Advanced Light Source, Lawrence Berkeley Lab. The Laue patterns obtained by this technique reveal that the laser-written crystal is similar to a plastically deformed crystal, comprising of tilt dislocation walls. Apparently, these dislocations are introduced to accommodate the mismatch between the density of the crystal and glass matrix, which in turn cause gradual rotation of the crystal lattice about the axis that is in the plane of crystal surface and normal to the laser writing direction. Preliminary results indicate that the magnitude of rotation per unit length of the crystal line depends on the orientation of the crystal lattice relative to the laser scanning direction, at least for the Sb-S-I system, and there may be a particular orientation for which its value is negligible. Confirmation of this observation in the future will provide conditions for fabricating single-crystal lines of fixed orientation through the whole length.

Group IV Nanomembranes, Nanoribbons, and Quantum Dots: Processing Characterization and Novel Devices

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Funding:	\$467,188 (2014)

PROGRAM SCOPE

Single-crystal semiconductor sheets present a platform for entirely new science and technology. They may form the basis for devices relevant in energy harvesting, transformation, and conservation. The novelty of thin crystalline sheets lies in the following. 1) They are thin; a factor that brings many new phenomena. The very high interface-to-volume ratio makes surfaces or interfaces, and their chemical and structural properties, very important contributors to unique membrane electrical, thermal, and mechanical behavior. 2) Thin sheets can be strained to a high degree, effectively allowing lattice constant choice. Many of the most fundamental materials properties are influenced by the lattice and distortions of the lattice. 3) They are easily stackable and bondable, introducing the potential for an entirely new set of composite materials that change their properties vertically on the scale of 10s to 100nm. Because of this property, interface effects can be significant, but are readily investigated. Additionally, sheets are compatible with all top-down processing that is conventional in the

semiconductor device industry. The platform of single-crystal semiconductor sheets offers the choice of nano-size in one, two, or three dimensions, as well as the formation of structures with mixed dimensions, but the true advantage is working at the nanoscale in one dimension, while the other two dimensions are at the mesoscale or macroscale. Our work provides excellent prospects for modifying and enhancing materials properties, and new areas of nanomembrane (NM) processing that can act as technology drivers.

FY 2014 HIGHLIGHTS

Research has focussed on composites of thin nanomembranes, some of crystalline/crystalline combinations, some on crystal/polymer combinations. An example of the first is graphene on Ge, with outstanding, record values of charge transport measured in graphene due to interface effects. An example of the latter is Si NMs on PDMS, creating novel microstructures that are useful in bioengineering or fluidics sensing. Other combinations include SiN_x thin films on a free-standing Si NM, to explore mechanical properties associated with film formation, and thin SiGe NM single crystals to serve as seeds for strained-Si two-dimensional electron gases (s-Si 2DEGs). 13 papers were published in 2014 with partial or exclusive support from this grant.

Hydrogen Caged in Carbon-Exploration of Novel Carbon-Hydrogen Interactions

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

Our research includes four complementary projects. The first two utilize Diels Alder condensation reactions to attempt to trap hydrogen in carbon cages via 'wrapping' and/or polymerization of carbon around available hydrogen, focusing on extreme pressures of model compounds in a diamond anvil cell. The third project probes hydrogen penetration into known and well-characterized carbon materials under extreme conditions; in the past year this has focused on correlation of spectral features and perturbations in model carbon structures and gas diffusivity. The fourth modeling project probed candidate carbon structures that may form in the three experimental projects. In addition to these four original project lines, we added a fifth line of research concerning the formation of carbon-hydrogen interactions when hydrogen is provided via an adjacent transition metal catalyst.

FY 2014 HIGHLIGHTS

Gas confinement via repulsive interactions is intended to design molecular-level nanostructures that act as compressed gas storage tanks. Under extreme conditions of pressure, hydrogen solubility in carbon materials is expected to increase and carbon is expected to restructure to minimize volume via a mixed sp²/sp³ hydrogenated state. High pressure polymerization of triptycene, a molecule with internal free volume, led to an amorphous hydrogenated carbon with 40% sp³ C-H content and retention of bridgeheads and rigidity. We have also probed near-ambient temperature confinement of N₂ and H₂ in model carbon geometries with spectroscopy and gas diffusivity measurements, with alteration of pore

geometry via synthesis and post-synthesis techniques. Defected carbon nanoshells did not retain gas at room temperature, even after deposition of amorphous carbon at the defects. A high binding energy (0.16 eV) interaction between N₂ and a porous polymer was observed at room temperature that was a function of pore dimension, which led us to revisit how spectra may be used as a means to characterize pore geometry in carbon materials, enabling rapid characterization of microgram quantities of sample. We are validating the technique for slit and cylindrical carbon geometries as a function of temperature, chemical potential, and gas density and correlating the results to gas diffusivity. We have also explored gas entrapment in flexible metal-organic frameworks and noted an unusual non-Fickian response behavior.

Quasiepitaxial Growth of Organic Crystalline Thin-Films

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Funding: \$152,000 (2014)

PROGRAM SCOPE

The presence of excitons in organic semiconductors at room temperature distinguish them from traditional semiconductors, providing exceptional opportunities for manipulating energy in a range of structures from light emitting diodes, lasers, transparent photovoltaics, and optical switches. However, control over crystalline order, orientation, and defect formation is crucial to the fabrication and optimization of these excitonic organic electronics. The overarching goal of this project is to understand and explore bottom-up vapor-deposition routes to the growth of large-area organic single crystalline like films with controlled thickness through a combination of organic-organic interactions. The specific aims are to 1) map growth modes from the vapor phase for archetypal homo-epitaxial and hetero-quasiepitaxial systems, monitored with both real-time and *in situ* diffraction techniques; 2) elucidate predictive energetic design rules for multilayer sustained quasi-epitaxial ordering; and 3) model and understand energetically driven quasiepitaxial relationships. This understanding will enable a new class of organic electronics with unique excitonic tunability and will be used as a platform to study organic quantum wells, exciton confinement, and determine upper limits for energy transport.

FY 2014 HIGHLIGHTS

We have now realized the growth of the first set of heteroquasiepitaxial multilayer organic thin film crystals. These crystals are composed of incommensurate organic semiconductors with sustained azimuthal ordering and controlled orientation grown from the bottom up. By probing a range of molecular pairings with in-situ and real-time diffraction, we have confirmed that one of the driving forces behind this growth is the requirement of surface energy matching of the lowest energy crystalline planes, which is completely distinct from the requirements of lattice matching for inorganic epitaxial growth. This insight is helping to provide a more universal understanding of the key requirements for such remarkable growth that has been historically inaccessible. In addition we have extended our molecular dynamics simulations of surface diffusion to understand the kinetic dynamics of a full molecular series across a range of surfaces. Combined, these results demonstrate the starting criteria

for manipulating the bottom up growth of multilayer organic thin-film crystals that is now being used as a platform to characterize energy transport in unique crystalline organic ensembles.

Non-Equilibrium Effects in the Processing of Materials Using Plasmas

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Funding: \$100,000 (2014)

PROGRAM SCOPE

The scope of this project is to investigate the interaction between nanoparticles and non-thermal plasmas. Dusty plasmas are emerging as a powerful and versatile tool for nanopowders synthesis, with several demonstration of successful production of semiconductor, metallic and even ceramic nanoparticles. While significant effort has already been given to plasma-induced chemical nucleation of dust and to the electrostatic charging of particles in plasmas, it is unclear how a non-thermal process can produce high-quality crystalline powder even for the case of high-melting point materials. This project addresses this issue. The main goal is to measure the temperature of nanoparticles as they are dispersed in a partially ionized gas. This can be achieved using several strategies, but this particular project relies on the use of in-situ FTIR to probe the nanoparticle surface as they are in direct contact with the non-thermal plasma. An IR beam is sent through the discharge as it is nucleating and growing nanoparticles. Under consideration is the case of a silane-containing plasma, which leads to the formation of silicon nanoparticles. By monitoring the stability of different surface moieties as the particles interact with the discharge it is possible to extract the nanoparticle temperature. Ultimately this project will provide a more detailed description of the interaction between particles and plasmas, focusing in particular on the complexity of the plasma chemistry and on its influence on the heating of nanoparticles during processing. This in turn will clarify what is the real potential of non-thermal plasma techniques for nanopowders synthesis and processing.

FY 2014 HIGHLIGHTS

This project led to two publications in 2014. The first one [1] summarizes an experimental study on the kinetics of phase change for ultrafine silicon powder. A second publication [2] discusses the kinetics of crystallization of silicon particles when exposed to a plasma instead of to a thermal source such as a furnace. Nanoparticles were grown in a non-thermal plasma and sampled at different positions in the reactor using an extraction orifice). The structural evolution is monitored as a function of residence time in the plasma. In-situ FTIR is used to monitor the nucleation process and the nanoparticle surface. It is found that particles are first nucleated with an amorphous phase and then annealed by the plasma to reach a crystalline structure. By using the crystallization rate determined in [1] it is possible to calculate the necessary temperature to which the particles should be heated to observe a phase transformation. This is found to be 1100K. Consistently with this measurement, the nanoparticle surface is bare as they are in the plasma, likely because of rapid thermal desorption. This work was presented at the AVS 61st meeting in Baltimore (invited talk). 1. Lopez, T. and L. Mangolini, 2014, *Nanoscale*, 6(3): p. 1286-1294. 2. Lopez, T. and L. Mangolini, 2014, *Journal of Vacuum Science & Technology B*, 32(6): 061802-1 to 8.

Thermochemistry of Oxides with Electrochemical and Energy Applications

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Funding: \$200,000 (2014)

PROGRAM SCOPE

This project represents a renewal, continuation, and redirection of a program emphasizing the thermodynamics of materials relevant to energy. The major objectives are: (a) to advance and use unique calorimetric capabilities to determine the energetics of oxide materials relevant to energy applications, with an emphasis on new materials for batteries and fuel cells, (b) to understand, in terms of both macroscopic energetics and microscopic structure and bonding, the interplay of defect chemistry, oxidation-reduction, and size effects at the nanoscale in determining the properties of oxides. In addition to completing work on ionic conductors and continuing to pioneer calorimetric studies of refractory materials above 1500 °C, this project will emphasize mixed ionic - electronic conducting materials containing transition metals of variable valence, especially perovskites ($A_xRE_{1-x}M_yM'_{1-y}O_3$ (A = alkaline earth, RE = rare earth, M and M' = Mn, Fe, Co) and lithium containing rocksalt, spinel, olivine, and fluorosulfate phases with M = Mn, Fe, Co, Ni. In addition, thermochemical studies of purely ionic conductors (Bi_2O_3 - based fluorite structured electrolytes, co-doped rare earth ceria, apatites) will be continued. The major and unique technique employed is high temperature oxide melt solution calorimetry, with careful attention to materials synthesis and characterization. Direct *in situ* studies of refractory oxides above 1500 °C by levitation melting and crystallization, synchrotron – based diffraction, and improved differential scanning calorimetry will probe structure and phase transitions in refractory oxides.

FY 2014 HIGHLIGHTS

We have made progress on several fronts. Salih Buyukkilic has completed his Ph.D. and is starting a job at Intel. The second half of his thesis work involved the high temperature thermochemical and conductivity behavior of neodymia and samaria singly and co-doped ceria. We have shown definitively that the correlation between maximum heat of mixing and highest ionic conductivity holds up to 700 °C, with the composition of the maximum shifting to higher dopant concentration, consistent with increasing defect dissociation at higher temperature. This work is being prepared for publication. S. Mahboobeh Hosseini, working on apatites, completed her Ph.D. and is now employed by Chevron. An additional paper is published and another is under review. Tien Tran, postdoc, is now teaching at the University of the Pacific. A paper showing the effect of order-disorder on the thermodynamics of doped bismuth oxide has been published. Our work on battery materials is our exciting new focus. We have shown that $LiCoO_2$ has low surface energy and low hydration energy and argue that these features are important in aiding ion and electron transfer across the electrode/electrolyte interface. The results support theoretical calculation by Meng's group. Our work is recently published in *Angewandte Chemie* (Maram *et al.* 2013). In addition, we have finished work on a set of hydroxysulfate ionic conductors from Tarascon's group in France. The paper is in the final revision stages for publication. Selected Publications include: 'Energetic Effects of Substitution of La-Nd and Si-Ge Oxyapatite-Type Materials' S. M. Hosseini and A. Navrotsky, *J. Am. Ceram. Soc.*, 96, 3915-3919 (2013). "Energetics of Disordered and Ordered Rare

Earth Oxide-Stabilized Bismuth Oxide Ionic Conductors” T. Tran and A. Navrotsky, Phys. Chem. Chem. Phys., 16, 2331-2337 (2014).

A Fundamental Study of Inorganic Type II Clathrate Open-Framework Materials

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

The goal of this project is to investigate the intrinsic properties of intermetallic clathrates in order to develop fundamental structure-property relationships that expand the knowledge base of the unique properties that these materials possess. The intellectual merit of investigating these materials is very closely tied with their novel structure and the corresponding physical properties they exhibit. This work is intended to lead to a clearer understanding of the unique properties that define the suitability of these materials for energy-related applications. New processing and crystal growth techniques are also of interest due to the fact that for many materials of technological interest, as well as materials that probe fundamental new physical phenomena, the preparation of high-purity compositions, or high-quality single crystals, by traditional techniques is very challenging. This research has allowed for strong collaborations with other DOE-funded experts and their research groups (e.g. Prof. Carolyn Koh at the Colorado School of Mines) as well as international researchers in the field (e.g. Prof. Dr. Yuri Grin, Director, Max Planck Institute for the Physical Chemistry of Solids).

FY 2014 HIGHLIGHTS

Intermetallic clathrates continue to be of scientific and technological interest, however, the synthesis of phase pure clathrates, new compositions in particular, is extremely challenging especially when the component elements possess significantly different melting points and/or vapor pressures. New synthetic approaches are therefore a major part of this research project. We employed two new methods for crystal growth developed under this DOE project, spark plasma sintering (SPS) and kinetically controlled thermal decomposition (KCTD), in investigating intermetallic clathrates of different compositions as well as new “open-framework” materials, some for the first time. For example, $K_8Ge_xSi_{46-x}$ with varying Ge content (x) and $Na_8Al_ySi_{46-y}$ with varying Al content (y) were synthesized for the first time. The former was synthesized employing KCTD and the later SPS. Optical and transport properties investigations revealed that $Na_8Al_8Si_{46}$ is a semiconductor with properties that may be of interest for thermoelectrics applications. In expanding on the use of SPS for materials synthesis, single crystals of a new ternary type-II clathrate, $K_6Na_{16}Si_{136}$, as well as $Rb_8Na_{16}Si_{136}$ and $Cs_8Na_{16}Si_{136}$ clathrates were synthesized by using a mixture of NaSi and AlCl (A = K, Rb and Cs) as the precursor for ion-exchange/electrochemical redox reactions by SPS. This novel synthetic approach indicates that SPS can be employed in topochemical ion exchange reactions, thus allowing for the rapid synthesis of single crystals of multinary intermetallic phases that cannot be accessible by traditional crystal growth techniques. In addition, a novel solution oxidation approach employing ionic liquids was employed in the synthesis of clathrates. Three uniquely different synthetic and crystal growth techniques were therefore developed under this project.

Fundamentals of Spark-Plasma Sintering: Material Processing for Energy Applications

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Funding: \$253,000 (2014-2015)

PROGRAM SCOPE

The program is focused on the development of a multi-scale theory of spark-plasma sintering (SPS) of powder components. SPS is a rapidly emerging powder consolidation technique capable of producing highly dense materials with a significant potential for grain size retention. Potentially, SPS has many significant advantages over the conventional powder processing methods, including the lower process temperature, the shorter holding time, dramatically improved properties of sintered products, low manufacturing costs, and environmental friendliness. Practical implementations of the SPS' bright potential, however, are limited by the lack of theoretical concepts enabling the process predictiveness and optimization. The project introduces important mechanisms of both thermal and non-thermal nature in a novel generic micro-macro modeling framework for the description of spark-plasma sintering. The modeling activities are supported by unique experiments on the de-convolution of the heating rate-driven and electromagnetic field-imposed effects at various scale levels. The developed concepts are implemented in a novel multi-scale modeling framework describing spark-plasma sintering for the optimization of the fabrication of functional porous structures of nuclear fuel for modular multiplier reactors. Thereby, the main applied aspects of the project are concerned with exploring the previously non-investigated applications of spark-plasma sintering to the fabrication of structurally strong porous materials, which are of great interest for nuclear fuel and other energy-related applications. The collaborative component of the proposed program involves interactions between San Diego State University and General Atomics - one of the world's leading resources for the high-technology systems development.

FY 2014 HIGHLIGHTS

During the reported period the following major research results have been obtained: (I) By solving a number of problems to determine the micro-nonuniform temperature distribution in resistance heating of a copper powder with spherical particles, it was shown that the contact temperature may be substantially different from the average macroscopic temperature of the sample, up to melting of the contact upon slight increase in macro-temperature. (II) Inter-particle neck growth kinetics of vanadium carbide powder during initial stages of conventional and spark-plasma sintering has been investigated. The neck sizes derived from scanning electron microscopy observations were utilized in the inverse regression of the surface diffusion equation and led to the calculation of the value of the surface diffusion activation energy for the vanadium carbide powder. (III) The SPS overheating phenomenon was analyzed by varying the geometry of the tooling that exhibits the problem, namely by modeling various tooling configurations involving sequences of disk-shape spacers with step-wise increasing radii. The analysis was conducted to obtain a more suitable SPS tooling configuration with the avoidance of the overheating as a final aim. (IV) Fe, Ti powders and their mixtures were subjected to electric discharges in a hydrocarbon liquid. The obtained powder mixtures were consolidated by spark plasma sintering. The densification behavior, microstructure, phase composition and mechanical properties of the processed

powder samples were investigated. The developed fabrication approach represents a novel technological route for metal-ceramic powder composites' fabrication where the electromagnetic field assistance is employed at both powder synthesis and powder consolidation stages. The research results have been published in a number of refereed journals including Scripta Materialia, Intern. Journal of Refractory Metals and Hard Materials, Adv. Engineering Materials, and Materials.

Plasmonic Control of Radiation and Absorption Processes in Semiconductor Quantum Dots

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Funding: \$170,000 (2014)

PROGRAM SCOPE

This project is focused on the control of radiation and absorption processes in semiconductor photonic materials through the use of metallic nanoantennas. By virtue of their strongly confined plasmonic resonances, these nanostructures can concentrate incident radiation into sub-wavelength "hot spots" of highly enhanced field intensity, thereby increasing optical absorption by suitably positioned nanoscale absorbers. By reciprocity, the same nanoparticles (NPs) can also dramatically increase the spontaneous emission rate of radiating dipoles located within their hot spots. In this case, the far-field properties of the emitted light (e.g., polarization and directionality) are also determined by the nature of the plasmonic excitations involved in the radiation process. The NPs can therefore be used to enhance the light-emission efficiency of the underlying active material and at the same time control the output radiation far-field pattern. The study of these phenomena can address a number of basic questions related to the optical properties of metallic nanostructures, while at the same time pave the way to new device concepts, e.g., for sensing, optoelectronics, and photovoltaics. The specific semiconductor samples employed in this project involve quantum structures based on the InGaN materials system. While earlier work has focused on quantum wells, the use of highly localized quantum dots (QDs) is currently being pursued, which will allow us to directly probe the giant optical-field enhancements produced by metallic NPs in their hot spots. InGaN QDs are also promising for the demonstration of high-efficiency photovoltaic energy conversion based on the intermediate-band device concept – a potentially transformative application which could benefit strongly from the proposed plasmonic interactions. Thus, another important goal of this research is the demonstration of plasmon-enhanced light absorption via both interband and intraband transitions in InGaN QDs.

FY 2014 HIGHLIGHTS

The research activities carried out during FY 2014 have mostly focused on the development of high-quality InGaN QD samples with small dimensions (to enable fully three-dimensional quantum confinement) and high In content (to red-shift the bandgap energy into the green spectral region and beyond). Both of these conditions are particularly important for the intermediate-band photovoltaic application just described. The QD samples were grown using epitaxial self-assembly techniques based on the Stranski-Krastanov growth mode, and characterized using x-ray diffraction, AFM, SEM, and optical measurements. The results of these studies indicate that the QD optical properties are suitable to the investigation of the proposed plasmonic interactions. In particular, photoluminescence as well as

absorption due to transitions between quantum confined states in the QDs were observed. Regarding the metallic nanostructure development, a particularly significant outcome has been the demonstration of plasmonic beaming with simultaneously enhanced output light intensity. In prior work within this project, metallic nanoantenna arrays on InGaN quantum-well samples were developed to produce highly collimated radiation beams emerging from the sample surface along predefined geometrically tunable directions. At the same time, however, the total radiated power (i.e., integrated over all directions) was found to be somewhat reduced by the presence of the beaming nanostructures, due to optical losses in the metallic ground plane supporting the nanoantenna array. During the current reporting period, the array geometry has been modified to overcome this drawback, leading to the initial demonstration of plasmon-enhanced light emission combined with plasmonic beam shaping.

New Oxide Materials for an Ultra High Temperature Environment

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Funding: \$150,000 (2014)

PROGRAM SCOPE

The development of ceramics that provide a robust performance in an aggressive high temperature environment is a continuing challenge. The available ceramics such as zirconates, sialons, diborides or carbides satisfy some of the requirements such as high melting temperature, but they also exhibit limitations such as a high oxidation rate or surface decomposition especially in the presence of water vapor. What is needed for enhanced high temperature capability are new oxide materials. From the existing experience we are pursuing a new strategy that involves internal modification control of the outer surface of diborides to promote enhanced oxidation resistance. The internal modification focuses upon the development of a new oxide type based upon HfTaO ($n\text{HfO}_2 \cdot \text{Ta}_2\text{O}_5$, $5 \leq n \leq 7$) and ZrTaO superstructures which lowers the oxidation rate. The oxide superstructures are metastable in the binary Hf-O and Zr-O systems, but experiments confirm that they can be stabilized by Ta additions. The primary objective is to establish an understanding of the synthesis and performance of a new oxide materials class based upon HfTaO and ZrTaO superstructures. This includes: (1) synthesis of (Hf, Ta)_{B₂} multicomponent borides and the use of Hf-Ta alloys and the diboride as precursors to synthesize the HfTaO superstructures by high temperature oxidation; (2) evaluation of the phase stability at high temperature up to 2500°C and measurement of selected thermodynamic properties (i.e. C_p and α) by a differential scanning calorimeter (DSC) and high temperature XRD; (3) quantitative assessment of the oxidation resistance of the multicomponent borides and oxide superstructures by Thermal gravimetric analysis (TGA), measurement of weight change and oxide thickness to identify the oxidation mechanisms and synthesis kinetics of the multicomponent oxide superstructures. In addition to the primary objective, we also intend to evaluate the potential of the superstructures to develop low thermal conductivity.

FY 2014 HIGHLIGHTS

We have synthesized pure HfTaO oxides superstructures by fully oxidizing Hf-27Ta and Hf-35Ta alloy precursors. We have discovered a novel synthesis mechanism for the formation of the HfTaO

superstructures. During exposure to oxygen at high temperature (e.g. 1500°C) the initial homogeneous BCC solid solution dissolves oxygen. Next, the BCC phase with oxygen in solution undergoes a phase separation reaction to yield two BCC phases: a Hf-rich phase and a Ta-rich phase with both phases containing oxygen in solution. With continued exposure the oxygen content in the BCC phases increases to the level necessary to initiate the formation of monoclinic HfO₂ and orthorhombic Ta₂O₅. Lastly, the monoclinic HfO₂ is converted to a cubic structure and with further reaction the HfTaO orthorhombic superstructure is established at the outer surface region. To determine if this reaction pathway occurs in other systems we have examined the oxidation of a Zr-20Nb alloy and have confirmed a similar reaction sequence leading to the synthesis of ZrNbO superstructures. We also found that the Hf-27Ta alloy exhibits parabolic kinetics with a parabolic rate constant that is over 20 times lower than that for Hf at 1200°C. By using the pure HfTaO superstructures, we demonstrated that the HfTaO oxide superstructures are stable up to over 1800°C in air. The heat capacity of HfTaO at 1650°C was measured as 63.85 J•mol⁻¹•K⁻¹, which is much smaller the value of ZrO₂ (81.1 J•mol⁻¹•K⁻¹); thus, the HfTaO superstructure may have a lower thermal conductivity than ZrO₂. We have also successfully synthesized (Hf,Ta)B₂ borides by reaction synthesis. The formation enthalpies of HfB₂ and TaB₂ are (-328.9 kJ/mole) and (-209.2kJ/mole) respectively. Upon heating a well-mixed and compacted sample of elemental powders, the initiation of diboride formation is rapid and the adiabatic temperature rise is in excess of the diboride melting temperatures to enable formation of the diboride solid solution.

Phase Transformations and Equilibria in Complex Half-Heusler/Full-Heusler Nanocomposites

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 Funding: \$340,000 (2014)

PROGRAM SCOPE

This project focuses on experimental and theoretical investigations of the mechanisms of phase formation and transformations in various half-Heusler/ full-Heusler systems. The resulting HH_(1-x)/FH_(x) nanocomposites are structural characterized using a combination of X-ray diffraction and transmission electron microscopy. Finally, the mechanism by which FH nanostructures regulate electronic and thermal charge transport in the synthesized nanocomposites is investigated using a combination of transport and microstructural data.

FY 2014 HIGHLIGHTS

During the past four quarters of the project, we focused our attention on the synthesis, structural characterization, and evaluation of the thermal and electronic transport in p-type Ti_{0.5}Hf_{0.5}Co_{1+x}Sb_{0.9}Sn_{0.1} and n-type Ti_{0.1}Zr_{0.9}Ni_{1+x}Sn_{0.975}Sb_{0.025} nanocomposites. In addition, we have investigated the effect of synthesis and processing methods on the microstructure and electronic transport of bulk nanostructured half-Heusler phases and also obtained preliminary results on the theoretical investigation of the formation of full-Heusler precipitates in TiNiSn half-Heusler matrix. We show that *in situ* growth of coherent nanometer-scale full-Heusler (fH) quantum dots (fH-QDs) within the p-type Ti_{0.5}Hf_{0.5}CoSb_{0.9}Sn_{0.1} half-Heusler (hH) matrix induces a drastic decrease of the effective hole density

within the hH/fH-QD nanocomposites at 300K followed by a sharp increase with rising temperature. This behavior is associated with the formation of staggered heterojunctions with a valence band (VB) offset energy, ΔE at the hH/fH phase boundaries. The energy barrier (ΔE) discriminates existing holes with respect to their energy by trapping low energy (LE) holes, while promoting the transport of high energy (HE) holes through the VB of the fH-QDs. This “hole culling” results in surprisingly large increases in the mobility and the effective mass of HE holes contributing to electronic conduction. The simultaneous reduction in the density and the increase in the effective mass of holes resulted in large enhancements of the thermopower whereas; the increase in the mobility minimizes the drop in the electrical conductivity. [1] Pranati Sahoo, Yuanfeng Liu, Julien P. A. Makongo, Xian-Li Su, Sung Joo Kim, Nathan Takas, Hang Chi, Ctirad Uher, Xiaoqing Pan, Pierre F. P. Poudeu*, Full-Heusler nanostructures Boost Thermopower and Hole Mobility in Bulk p-type Half-Heuslers, *Nanoscale* 2013, 5, 9419-9427.

Improved Electrochemical Performance of Strained Lattice Electrolytes via Modulated Doping

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

Solid electrolytes, found in batteries, fuel cells, and chemical sensors, are highly (and increasingly) important energy technology components. Nevertheless, the rigid atomic framework of solids provides for relatively few materials with high ionic conductivity, particularly at low temperatures. For example, solid oxide fuel cells typically must be operated at ≥ 800 °C in order to obtain sufficient oxygen ion conduction through the electrolyte. These temperatures necessitate the use of expensive components and limit device lifetimes, making them economically unfeasible at this time. Recently, the use of nanostructured multilayers has been proposed as a means to obtain vastly improved solid state ionic conduction. Unfortunately, the experimental evidence advocating these techniques has often been controversial. In addition, nearly all of the multilayers demonstrated have used layer materials wherein one of the layers was a poor ion conductor. In this project, we have sputter deposited nanostructured, pseudo-homoepitaxial multilayers of oxygen ion conductors. Impedance spectroscopy has been used to determine the effects of the spacing and magnitude of compositional (and therefore lattice parameter) modulation on the ionic conductivity. In addition, ionic analogues of the high electron mobility transistor (HEMT) were formed by modulation of the dopant and host atom concentrations, thereby forming high ionic mobility electrolyte layers in close proximity to layers with high dopant (and thus defect) concentration. Important discoveries made in this project include the ability to use heterogeneously distributed dopants to improve oxygen ion conduction in cerium oxide electrolytes and quantification of the linear strain effect on oxygen vacancy mobility, among others. Oxygen ion conductors, with application to SOFCs, were used in this study; however, the concepts and methods discovered are believed to carry over to other ionic conduction systems.

FY 2014 HIGHLIGHTS

This project previously found that 100 nm or thicker yttria-stabilized zirconia (YSZ) films exhibited lattice parameters and oxygen ion conductivities similar to bulk samples, but that lattice strain and increased

ion conductivity resulted as the thickness decreased to 6 nm. This project year found that these thinnest films exhibit a second significant conduction mechanism. Specifically, we showed for the first time that in humid environments, proton conduction along the free surface of ultrathin YSZ can become comparable to oxygen ion conduction through the volume, even > 200 °C. Building on prior project year's discovery that alternating nanolayers of pure Y₂O₃ and pure CeO₂ yields ion conduction in space charge regions at the interface, the effects of dopant type were examined during this project year. The Gouy-Chapman model previously implemented to describe space charge region conduction had to be generalized, as it could not account for significant differences in conductivities as the Y₂O₃ was replaced with Gd₂O₃ and La₂O₃. Promisingly, we showed for the first time that heterodoped ceria can support a low activation energy of conduction despite high overall dopant concentration, improving the low temperature conductivity relative to other dopant strategies. Finally, nanostructured multilayers of ceria-zirconia interleaved with either doped ceria or YSZ were fabricated and characterized. The multilayers with doped ceria showed strain was effectively created, with the ceria compressed by up to 2.2% and with concomitant ionic conductivity reductions by a factor of as much as 3. This project thus provides some of the most unambiguous evidence of a strain-ionic conductivity relationship to date. Multilayers with YSZ exhibited non-elastic accommodation of the lattice mismatch, and no change in conductivity was observed. The past year's project work has resulted in 8 peer reviewed papers and the PhD conferral on both supported students.

New Optoplasmonic Materials for Next Generation Energy Systems

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Funding: \$160,000 (2014)

PROGRAM SCOPE

This project develops new classes of optoplasmonic materials that amalgamate the advantages of conventional photonic and plasmonic electromagnetic materials. Optoplasmonic materials provide unique opportunities for enhanced light capture and energy transfer/storage through the availability of delocalized photonic-plasmonic modes. These opportunities can be translated into custom-designed optoplasmonic materials for a variety of applications, including enhanced light absorption and generation of carriers in semiconductors, enhanced light processing and transfer, and controlling cooperative interactions of atomic and molecular systems. However, a precise understanding of the, as yet unknown, electromagnetic coupling mechanisms underlying the near- and far-field optical properties of these mixed metal-dielectric materials is required to achieve these goals. The overarching theme of this project is the development of this understanding for morphologically well-defined networks and extended two-dimensional arrays of noble metal nanoparticles and dielectric resonators. Electromagnetic interactions between the photonic (dielectric particles) and plasmonic (noble metal nanoparticles) building blocks in the resulting multi-scale structures can be manipulated to create a collective photonic-plasmonic response which is more than just the simple summation of the properties of the individual components. Rationally designed optoplasmonic materials hold the potential to pave the road to entirely new device functionalities. Optoplasmonic materials with custom tailored optical responses that can localize, enhance, and transfer the incident light with high spatial control could, for instance, enhance light conversion efficiencies across the entire visible range and beyond. We focus in

this project on the development of reliable fabrication approaches to implement and test these novel materials and then elucidate their physical working principles.

FY 2014 HIGHLIGHTS

We have developed new colloidal assembly techniques that facilitate the integration of electromagnetically strongly coupled plasmonic clusters and colloidal high refractive index materials (e.g. TiO₂ nanoparticles) into optoplasmonic hetero-nanoparticle arrays. The developed fabrication tools provide control over interparticle separations from a few to hundreds of nanometers, which provides important degrees of freedom for tuning near- and far-field optical responses as well as tailoring the optical phase landscape. We were able to demonstrate – experimentally as well as through electromagnetic simulations – that these new materials give rise to a cascaded electromagnetic field enhancement when delocalized photonic array resonances couple to localized surface plasmon resonances of the plasmonic nanoparticle clusters. Importantly, the photonic-plasmonic mode coupling did not only affect the electromagnetic hot-spots located in the metal nanoparticle clusters, but also achieved a general increase of field intensity throughout the array. The generation of an increased electromagnetic field enhancement in the entire array is an important step towards the engineering of homogeneously “hot” surfaces for enhancing light-matter interactions in a large volume of the ambient medium. In a subsequent step of this work we have refined our fabrication strategies to allow the combination of gold nanoparticles with high refractive index silicon nanoresonators. The coupling of plasmonic antenna and high refractive index silicon allows a coupling of electronic and magnetic resonances and we were able to show that metal-silicon hybrid resonators achieve a dramatic radiative rate enhancement with defined spatial emission properties. We have also demonstrated an on-chip photon transfer over several microns in networks of optoplasmonic structures made of whispering gallery mode resonators (dielectric microspheres) containing plasmonic antennas in their equatorial plane.

Using Interfaces to Create Strongly-Coupled Magnetic-Ferroelectrics via Atomic-Scale Heteroepitaxy

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Funding: \$680,000 (2014)

Jointly funded by “Electron and Scanning Probe Microscopies” and “Synthesis and Processing Science”

PROGRAM SCOPE

Our objective is to create a ferromagnetic ferroelectric that can be deterministically switched between symmetry equivalent states using an electric field. The electric-field switching of a magnetization between 180° symmetry equivalent states has not been demonstrated in any material. The required coupling between ferroelectric and ferromagnetic domains allowing such switching is a missing feature in most multiferroics and is key to advancing the field both scientifically and technologically. Starting at the level of electrons and atoms our goal is to rationally design complex oxide heterostructures and interface-materials with this targeted emergent behavior. Using a combination of symmetry arguments and first-principles calculations to explore the connection between structural distortions and

ferroelectricity in the perovskite family of materials, we have predicted electrical control of magnetism in the hexagonal rare earth ferrites. These realizations are created with atomic-layer precision, microscopically interrogated to see if there are competing mechanisms to the intended realization, and finally their macroscopic properties are measured. Here we will develop the scientific ideas and experimental tools necessary to apply this design paradigm to the creation of multiferroics with unprecedented coupling between ferroelectric and magnetic order parameters.

FY 2014 HIGHLIGHTS

We have studied, both theoretically and experimentally, the properties of metastable hexagonal rare-earth ferrites with the $YMnO_3$ structure. In the hexagonal rare-earth manganites ($RMnO_3$), improper ferroelectricity (trimerization) leads to a network of coupled structural and magnetic vortices that induce domain wall magnetoelectricity and magnetization (M), neither of which, however, occurs in the bulk of these materials. It is relegated to the domain walls. Through a combination of first-principles calculations, group-theoretic techniques, and microscopic spin models, we have shown how the trimerization not only induces a polarization (P), but also a bulk M and bulk magnetoelectric effect. This results in the existence of a bulk linear magnetoelectric vortex structure or a bulk magnetoelectric coupling such that if P reverses so does M. We determined the intrinsic properties of the metastable hexagonal polymorph of $LuFeO_3$. We find that hexagonal $LuFeO_3$ is a canted antiferromagnet with $T_N=147$ K and a saturation magnetization, $M_s=0.018 \mu_B/Fe$. We have combined $LuFe_2O_4$ which is ferrimagnetic below 240 K, although it is not ferroelectric, with hexagonal $LuFeO_3$ that is a robust high-temperature ferroelectric with a closely related structure. The resulting precisely engineered $(LuFeO_3)_n(LuFe_2O_4)_m$ superlattices are strong ferrimagnet-ferroelectrics with the highest-known simultaneous transition temperatures. Using scanning transmission electron microscopy imaging and spectroscopy we have mapped the structure, chemistry, and polarization of these artificial multiferroics. Our results show that the superlattices have a higher ferrimagnetic ordering temperature (T_C) than either of the end members, $LuFe_2O_4$ and $LuFeO_3$, from which they are created. T_C increases to nearly room temperature with simultaneous ferroelectricity, suggesting the tantalizing prospect of the existence of the world's first single-phase room-temperature ferrimagnetic ferroelectric.

Discovery and Crystal Growth of New Oxide Phases from Metal Fluxes

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Funding: \$200,000 (2014)

PROGRAM SCOPE

Discovery and growth of crystalline materials is one of the key areas in materials research. New materials, and engineering of their properties, have produced tremendous progress. The search for new materials with novel properties remains an ongoing activity. Of the many oxide single crystal growth methods, flux growth has proven to be an excellent method for exploratory synthesis work that also will yield crystals large enough for structural and physical characterization. Using metal fluxes to grow oxide phases produces a unique crystal growth environment, where oxygen is now a minority constituent. The low melting point of certain metal fluxes in use allows low temperature synthesis, and gives access to

potentially metastable and hard to crystallize phases. We are investigating single crystal oxide growth from alkaline earth metal fluxes, where the sizable oxygen solubility as well as good solubility of lanthanides is used to discover new phases. The reactivity of the flux can be tailored to provide reducing conditions for oxide growth by using alkaline earth mixtures, or the flux material can also be incorporated into the oxide. In particular, the low temperature eutectic mixtures of magnesium with calcium, strontium and barium provide control not only over crystal growth temperatures, but also the reactivity of the flux and its power to reduce lanthanide oxides. Furthermore, alkaline earth metal fluxes have simultaneous solubility for oxides, halides, hydrides, and chalcogenides; therefore new phases are expected to form under unusual conditions.

FY 2014 HIGHLIGHTS

The arrangement of lanthanide ions in the $BaLn_2O_4$ family of compounds ($Ln=La$ to Lu , Y) produces two trigonal ladders. The magnetic interactions of the lanthanide ions is thus expected to be frustrated, since the distances and angles in the Ln ladders are close to a regular triangle. The whole family of compounds was synthesized for the first time in single crystal form, allowing a detailed investigation of the structural changes induced by different sizes of the lanthanide ions. The magnetic properties of the series were further investigated, and geometric frustration has been observed. In the case of the prototypical $BaGd_2O_4$, the expected antiferromagnetic ordering temperature is around 10K, whereas the actual transition is at 2.7K. The two phases that indicate a high degree of frustration are $BaCe_2O_4$ and $BaYb_2O_4$. The former has one electron in the f-shell, whereas the latter has one hole in the f-shell. Structurally, the two ladders differ more in $BaCe_2O_4$ than in $BaYb_2O_4$, making $BaYb_2O_4$ more frustrated than $BaCe_2O_4$. Additionally, crystal field effects are observed in both compounds. A simple new phase has been discovered, Ba_2TeO , and Roxy-telluride, showing that a barium metal flux can have simultaneous solubility for oxygen as well as tellurium. The structure is a semiconductor, with a band gap of the order of 3eV, as measured by optical transmission, and confirmed by DFT calculations. The structure combines elements of the NaCl-type $BaTe$ and BaO structures: two layers of $BaTe$ alternate with one layer of Ba_2O_2 , forming a tetragonal layer structure. The in-plane compressive stress on the Ba_2O_2 layer results in the oxygen atoms moving out of the plane, giving a puckered Ba_2O_2 layer that is related to the inverse PbO -type structure. Testing of the barium flux for antimony and bismuth solubility, two new phases were discovered: $SmMg_2Bi_2$ and $SmMg_2Sb_2$. These compounds crystallize in the hexagonal Mg_3Sb_2 -type and may be potential thermoelectric materials.

Epitaxial Electrodeposition of Metal Oxide Thin Films and Superlattices for Energy Conversion and Storage

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PROGRAM SCOPE

Although the electroplating of metals is a mature technology, the electrodeposition of metal oxide ceramics is still in its infancy. The metal oxide films and nanostructures are electrodeposited by driving chemical reactions at electrode surfaces. It is a bottom-up processing methods in which solids are

assembled from molecules and ions in solution- much like biomineralization The focus of the project is the electrodeposition of metal oxide semiconductors, catalysts, and pseudocapacitor materials for energy conversion and storage. Specific topics we plan to explore are (i) electrodeposition of crystalline cobalt oxide- a potent oxygen evolution reaction, (ii) electrochemical reduction of epitaxial metal oxides to epitaxial metals and alloys, (iii) electrodeposition of nanostructured metal oxides for pseudocapacitors, and (iv) electrodeposited plasmonic nanostructures for photovoltaics. The research strongly emphasizes the basic science behind the electrodeposition of epitaxial and nanostructured metal oxides.

FY 2014 HIGHLIGHTS

Germanium is a group IV semiconductor with superior electronic properties compared with silicon, such as larger carrier mobilities and smaller effective masses. It is also a candidate anode material for lithium-ion batteries. This year, we introduced a one-step method to electrodeposit dense arrays of germanium nanowires onto indium tin oxide (ITO) substrates from aqueous solution. The electrochemical reduction of ITO produces In nanoparticles that act as a reduction site for aqueous Ge(IV) species, and as a solvent for the crystallization of germanium nanowires. Nanowires deposited at 95 °C have an average diameter of 100 nm, whereas those deposited at room temperature have an average diameter of 35 nm. Both optical absorption and Raman spectroscopy suggest that the electrodeposited germanium is degenerate. The high conductivity of the wires should make them ideal for lithium-ion battery applications. The results were published in ACS Nano. We also electrodeposited Co/CoOOH islands on n-Si to produce a photoanode for the photoelectrochemical splitting of water into hydrogen and oxygen. The n-Si/SiO_x/Co/CoOOH photoanode functions as a solid-state metal-insulator semiconductor (MIS) photovoltaic cell with spatially nonuniform barrier heights in series with a low overpotential water-splitting electrochemical cell. The results are under consideration for publication in Nature Materials.

Enhanced Materials Based on Submonolayer Type-II Quantum Dots

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Funding: \$209,000 (2014)

PROGRAM SCOPE

During the past few years we have investigated a nanostructured material known as sub-monolayer type-II QDs, made from wide bandgap II-VI semiconductors. Our goal is to understand and exploit their tunable optical and electrical properties, by taking advantage of the type-II band alignment and quantum confinement effects. Type-II ZnTe quantum dots (QDs) in a ZnSe host are particularly interesting because of their large valence band and conduction band offsets. In the current award we aim to develop enhanced materials based on these sub-monolayer type-II QDs, with emphasis on materials that may be advantageous for photovoltaic and spintronics applications. We also propose to expand the structural characterization of these materials by refining our X-ray diffraction methodologies. Last year we reported extensive work with ZnTe/ZnCdSe type II QDs materials that have

ideal properties for the development of intermediate band solar cells (IBSC). We also began a systematic approach to define the structural properties of these QDS, such as their size and their distribution, and began to investigate spin dynamics of these type II QDS. The past year we 1) developed new ways to analyze and model high resolution X-ray diffraction (HRXRD) techniques to extract structural details of sub-monolayer type II QD structures, 2) developed a model and made experimental validation of an approach to measure in-plane dimensions of the QDs and developed a model to calculate the dependence of QD size and density on the molecular beam epitaxy (MBE) growth conditions, 3) measured the linear polarization of the photoluminescence (PL) and confirmed the predictions obtained from HRXRD of anisotropic shape of the QDs, 4) made temperature dependent time resolved Kerr rotation (TRKR) studies to explore the spin dynamics of these materials, and 5) initiated studies of the growth of the so called "inverted" structure, in which the QDs are ZnSe and the matrix is ZnTe, which results in a material in which electrons are localized rather than holes.

FY 2014 HIGHLIGHTS

We previously reported high resolution X-ray diffraction (HRXRD) studies using a 1D model, in which the quantum dot (QD) layer was considered as a continuous layer, limiting the information that could be obtained. We have now used out-of-plane diffuse scattering and in-plane 3D mapping to obtain detailed structural information about the QDs. By performing small angle reciprocal space map around a reflectivity satellite, a 'fish bone' structure was observed, and related to the vertical correlation of QDs. 3D mapping presents a strong anisotropy in the diffuse scattering related to the QD shape. A QD elongation is seen in the $\langle 110 \rangle$ directions, consistent with anisotropy in the adatom mobility in the ZnSe surface. The shape of the QDs predicted by HRXRD should produce an optical anisotropy. To investigate this, we analyzed the linearly polarized PL emission. The collected PL intensity was found to be changing as we varied the analyzer angle, with the PL linearly polarized along the [110] axis of the sample, consistent with the anisotropy observed by HRXRD. The results obtained from PL and magneto-PL, HRXRD and secondary ion mass spectrometry data were combined to evaluate the QD density. We obtained the dependence of average QD volume and density on the Te flux and number of Te cycles, and show that these are the key parameters to control the QD dimension and distribution. The previously estimated radius of the stacked QDs was based on the assumption that the hole is strongly confined at the center of the dot. However, within the QD plane the Coulomb interaction between electron and hole should be much stronger than the quantization due to kinetic motion, and the trajectory of the hole is as important as that of electron. We have modified our model and applied a lateral tightly-bound exciton approach that takes into account the lateral wavefunction of the hole. The angular motions of the hole and the electron are strongly correlated, forming a well-defined dipole.

Directed Assembly of Rod-Coil Block Copolymers By Combined External Fields

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

The overall goal of this project is to understand, predict, and ultimately control the self-assembled nanostructures of rod-coil (RC) block copolymers in bulk, under thin-film confinement and with applied magnetic field. Photovoltaic (PV) energy obtained using conjugated (semiconducting) polymers is very attractive due to its cheap materials, low processing cost, and ease of large-scale manufacture. Control of the polymer morphology and structure at the nanoscale is critically important for optimizing the efficiency of polymer optoelectronic devices. The underlying hypothesis of this research is that such control can be achieved with magnetic-field directed assembly in thin films of RC block copolymers containing conjugated rod blocks. Using judiciously designed models and carefully selected methods, including 3D real-space parallel self-consistent field (SCF) calculations with high accuracy and newly proposed fast off-lattice Monte Carlo (FOMC) simulations with soft potentials that allow particle overlapping, we will examine in detail the effects of key factors (rod block length and volume fraction, RC incompatibility, orientational interaction between rod blocks, bending rigidity of rod blocks, and system fluctuations/correlations) on the self-assembled morphology of RC diblock copolymers (DBC) in bulk, as well as the effects of external conditions (surface preference, film thickness, substrate topology, and applied magnetic field strength) for obtaining the optimal structures of bulk heterojunction in RC DBC thin films optimal for PV cells. This research will allow knowledge-based rational design of these nanomaterials, instead of trial-and-error experiments in a large parameter space, which will advance their integration into a range of technologically important applications, including the fabrication of polymer-based PV cells, light-emitting diodes, field-effect transistors, and chemical and biological sensors.

FY 2014 HIGHLIGHTS

Based on the computationally efficient soft-core spherocylinder model for the orientational interaction between rod blocks previously developed and validated in this project, we have performed FOMC simulations to study the self-assembled morphology of RC DBCs in bulk as a function of rod block length and volume fraction, RC incompatibility, and orientational interaction between rod blocks. We have also developed efficient algorithms for the corresponding 3D real-space parallel SCF calculations based on the same model system used in our FOMC simulations, and examined the effects of system fluctuations/correlations by direct comparisons between FOMC and SCF results. These lead to two manuscripts being prepared for publication. We are currently working on the effects of external conditions on the morphology in RC DBC thin films.

Surface-Reaction-Limited Pulsed Chemical Vapor Deposition for Growing Nanowires Inside Highly-Confining Spaces

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Funding: \$210,000 (2013-2014)

PROGRAM SCOPE

The objective of this proposed research is to obtain in-depth understanding of the nanoscale crystal growth behavior in a surface-reaction-limited pulsed chemical vapor deposition (SPCVD) process, and thereby achieve well-controlled syntheses of three-dimensional (3D) nanowire (NW) arrays inside highly-confined spaces. In order to obtain in-depth understanding of the entire SPCVD process and eventually develop it into a versatile, highly controllable, and large-scale NW manufacturing technology, we propose an experiment-based project to study the nucleation and anisotropic crystal growth mechanisms of titanium dioxide (TiO_2) and extend it to the growth of other functional materials. The following four aspects will be investigated: (1) Study the atomic recombination and restructuring on TiO_2 crystal surfaces, and understand how a continuous polycrystalline atomic layer deposition (ALD) film is evolved into discrete NW arrays. (2) The window of this precursor-concentration-independent growth will be determined in order to perform valid SPCVD growth inside various 3D-confined spaces. (3) Understand how to apply SPCVD to other material systems including oxides (ZnO , In_2O_3 , SnO_2 , V_2O_5) and nitrides (GaN , AlN). (4) The pulsed precursor supply during SPCVD offers an opportunity to introduce impurity atoms (dopants) into the NW lattice. The doping mechanisms, dopant concentration control, and corresponding optical and electronic properties will be studied. This project will provide in-depth, experimentally grounded understanding of the nucleation and anisotropic crystal growth mechanisms of the SPCVD process. The outcome of this project will be a powerful NW synthesis technique that can uniformly grow NW arrays of controlled composition and morphology inside 3D-confined and submicron-sized spaces, thus enabling the creation of a variety of new functional nanomaterial architectures for the applications of electrochemical and photovoltaic electrodes, sensor elements, and catalysts.

FY 2014 HIGHLIGHTS

Our accomplishments during the report period include three aspects: (1) Observation of the Ostwald-Lussac Law in high-temperature atomic layer deposition (ALD). Through atomistic electron microscopy study of surface-reaction-limited pulsed chemical vapor deposition (SPCVD) TiO_2 nanostructures at designed growth cycles, we found that the evolution of TiO_2 nanostructures in ALD follows a path from amorphous layers to amorphous particles to metastable crystallites and ultimately to stable crystalline forms. Such a phase evolution is a manifestation of the Ostwald-Lussac Law, which governs the advent sequence and amount ratio of different phases in high-temperature TiO_2 ALD nanostructures. This discovery provides a new understanding of morphology and property variation, and phase non-uniformity in ALD thin films and nanostructures. (2) Observation of vapor-solid Kirkendall effect in ZnO-to- TiO_2 nanostructure conversion. Following our previous research on SPCVD of TiO_2 NRs on Si NWs, we explored the application of SPCVD of TiO_2 NRs on ZnO NWs. By introducing TiCl_4 vapor pulses to ZnO NW templates, we obtained TiO_2 nanotubes with well-preserved dimensions and morphology. This process involved the cation exchange reaction between TiCl_4 vapor and ZnO solid and the diffusion of reactants and products in their vapor or solid phases, which was a manifestation of the Kirkendall effect. This discovery offers a new route for hierarchical functional nanomaterial assembly and application. (3) Development of highly-efficient capillary photoelectrochemical (PEC) solar-fuel generation. 3D fibrous TiO_2 nanotube architecture was synthesized by ALD of TiO_2 films over cellulose nanofiber templates. In this design, capillary force could drive the electrolyte to the active area quickly and continuously. It mimics the mass transport process in natural photosynthesis, where the interaction between light and reaction sites is no longer limited by the volume, surface and depth of electrolyte.

Boron-Based Nanostructures, Stability, Functionality and Synthetic Routes

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Funding: \$510,000 (2014-2017)

PROGRAM SCOPE

This project goal is to advance our theoretical understanding of the boron assembly into nanoscale structures, initially ignited by the prediction of B_{80} fullerene. Theoretical modeling and assessment of possible structures and their properties, has then expanded towards the emerging area of two-dimensional (2D) materials and 1D nanowires. The project focus has been mainly on two important examples, representing in certain way two extreme cases: pure elemental B as most subtle and not yet synthesized in the laboratories, and h-BN-hexagonal boron nitride, a.k.a. 'white graphene'--a very stable compound with the array of useful properties available for experiments. In the meantime, a spectacular confirmation of pure boron Buckyball (B_{40} in recent report by the US-China collaborative team), has brought these exotic clusters back to focus. Extending the search to a broader spectrum of 2D boron-rich compounds whose synthesis can be rationalized, and properties can be explored in detail, constitutes the overall scope. Based on the first-principles computations, both synthesis and property characterization of several boron-rich nanostructures, including two-dimensional crystals of B_{12} , as well as novel layers of BC_3 , BSi, B_2O_3 , and B_xS_y composition, remain important lines of work.

FY 2014 HIGHLIGHTS

Motivated by experimental identification of B_{40} , recent comprehensive computational analysis revealed (i) mapping of B_{40} topological structure onto formal 2D-precursor monoatomic sheet; (ii) its instability with respect to dimerization and fusion; (iii) how it can be well isolated/preserved inside the inert carbon nanotubes or as adsorbed on graphene layer. Another class of pure-boron nanostructures are 1D linear chains, where density functional theory computations establish the possibility of a metastable (stable under tension) monoatomic chain $*B*B*B*B*$ (similar to C-chain carbyne!) and a free-standing more stable double-zigzag B-chain (with B_3 triangles serving as units). Electronic and mechanical properties, as well as chemical reactivity, establish the identity of these novel 1D-materials of boron. Among the boron compounds, one particularly important and recently synthesized is BN|C (coplanar BN with graphene) hybrid. Details of the optimal grain boundary interface structures are formulated in terms of tilt angle, lattice mismatch strain and deviation angle from the bisector line (reminiscent of Snell's law in optics), in good agreement with comprehensive numerical analyses. The ground state structures of the grain boundaries manifest as a series of laterally misaligned bisector segments, which are verified by intensive first-principle calculations. These findings not only provide a general guidance for exploring boundaries in various hybrid 2D materials but also serve as an important stepping stone for understanding mechanical and electronic behaviors in the boron-doped graphene and other hybrids.

Mapping the Synthetic Routes for 2-Dimensional Materials

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PROGRAM SCOPE

This project is motivated by three concurrent factors: (i) an intensified worldwide interest in two-dimensional (2D) materials, (ii) our laboratory's general approach to modeling the growth of graphene; (iii) emergent findings—including some in our own work—of specific functionalities among 2D materials, relevant to DOE interests, such as potential battery electrodes, catalytic activity, tunable energy band gaps for electronics, interfaces in heterogeneous systems for photovoltaics, etc. This raises broader compelling questions about the ways of making such monoatomic layers. The exfoliation from natural bulk precursors (3D bulk→2D layer) is not scalable. On the other hand, their synthesis—often called 'growth' due to visible change in size and shape—through chemical vapor deposition (CVD) involves complex gas-solid chemistry, which may work empirically, but its theoretical understanding and sentient design remain in infancy. This project will develop the state of the art multiscale models of 2D-layers on substrates, atomistic mechanisms of their nucleation (when the 2D island may or may not be preferred over the 3D cluster) and subsequent growth. Methods, from the first principles density functional theory to the nucleation and growth theories, organized in the nanoreactor mass-flow diagram, will be connected to larger-scale models (Monte Carlo, phase field, level sets). The focus on already established materials of interest, graphene (C), boron nitrogen (h-BN), transition metal disulfides like MoS₂, along with the emergent or even hypothetical borophene (B), phosphorene (P), stanene (Sn), and silicene (Si). Impact of this project, even if only successful for a subset of examples, could be enormous, leading to efficient synthesis of materials with novel desired properties. It will impact fundamental studies in this field, as well as permit various applications in devices, energy utility and production, of commercial and defense significance.

FY 2014 HIGHLIGHTS

The deep gap states created by defects in semiconductors typically deteriorate the performance of (opto)electronic devices. This has limited the applications of two-dimensional (2D) metal dichalcogenides (MX₂) and underscored the need for a new 2D semiconductor without defect-induced deep gap states. Comprehensive analysis has demonstrated that one 2D monoelemental semiconductor is a promising candidate. This is exemplified by first principles study of 2D phosphorus (P), a recently fabricated high-mobility semiconductor. Most of the defects, including intrinsic point defects and grain boundaries, are electronically inactive, thanks to the homoelemental bonding, which is not preferred in heteroelemental system such as MX₂. Unlike MX₂, the edges of which create deep gap states and cannot be eliminated by passivation, the edge states of 2D P can be removed from the band gap by hydrogen termination. It is further found that both the type and the concentration of charge carriers in 2D P can be tuned by doping with foreign atoms. This study sheds light on the role of defects in the electronic structure of materials, and how they can be made more energy efficient while also better performing in the devices.

Atomic Layer Deposition (ALD) of Metal and Metal Oxide Films: A Surface Science Study

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Funding: \$200,000 (2014)

PROGRAM SCOPE

The main objective of this research project has been to advance the fundamental knowledge of the surface chemistry of ALD precursors needed for the design and optimization of film deposition processes. A modern surface-science approach is being used to both elucidate the mechanisms of the reactions of the precursors on the surface and characterize the composition and morphology of the growing films. Special emphasis has been placed on: (1) Identifying the primary reactions that may lead to the deposition of clean films; (2) Identifying the secondary reactions that may help the ALD process, by, for instance, helping with the reduction (or oxidation) of the metal atom; (3) Identifying the secondary reactions that may lead to the deposition of impurities in the growing films; (4) Determining the kinetic parameters of the relevant surface reactions in order to define the optimum conditions for film deposition and to minimize impurity deposition; (5) Characterizing the nature of the resulting films, with focus on their stoichiometry and on the oxidation states of the elements; and (6) Using the information obtained to propose better precursors for given ALD processes. The depositions of two specific types of thin films relevant to microelectronics manufacturing are being studied here: (1) Transition metal films, Cu in particular, for electrical interconnects; and (2) Transition metal oxides and nitrides for diffusion barriers.

FY 2014 HIGHLIGHTS

The surface chemistry of bis[(N,N'-di-sec-butyl acetamidinate)Cu], the basis for our initial studies on Cu(110), was extended to investigate the differences in deposition with active metal surfaces such as Ni(110). A series of thermal stepwise conversions were identified, starting with the partial dissociative adsorption of the copper acetamidinate dimers into a mixture of monomers and dimers on the surface. An early dissociation of a C–N bond leads to the production of N-sec-butylacetamide, which is detected in the temperature program desorption (TPD) experiments in three temperature regimes, the last one centered around 480 K. Butene, and a small amount of butane, is also detected above approximately 500 K, and hydrogen production, an indication of dehydrogenation of surface fragments, is observed at 460, 550 and 670 K. All this chemistry shares common steps with that previously reported on Ni(110), but occurs at higher temperatures. The chemistry of second generation of acetamidinate precursors was also tested, tetrakis[Cu(I)-N-sec-butyl-iminopyrrolidinate] and bis[Cu(I)-N,N-dimethyl-N',N'-di-iso-propyl-guanidinate], on Ni(110). It was found that both precursors, which exist as tetramers and dimers in the solid phase, respectively, undergo dissociative adsorption at temperatures below 200 K to produce adsorbed monomers on the surface. A beta-hydride elimination step leads to the release of some of the ligands in dehydrogenated form at 300 K. The remaining adsorbates undergo similar decomposition between 350 K and 600 K as the copper atoms are reduced from a Cu(I) oxidation state to metallic Cu(0). Ethene and acetonitrile are produced from the Cu(I)-iminopyrrolidinate, and propene from the Cu(I)-guanidinate, and HCN from both. These results suggest a common behavior in the surface

reactions of these families of ALD precursors. Finally, we have also published several invited to write reviews on the subject of ALD.

EARLY CAREER: Utilizing Molecular Self-Assembly to Tailor Electrical Properties of Si Nanomembranes

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PROGRAM SCOPE

The program is focused on understanding the various interfacial phenomena, including self-assembly of organic molecules, charge injection, distribution, and separation at the organic–inorganic hetero-interface that control electronic behavior. Interfacing organic molecules with semiconductors, in particular, with semiconducting nanostructures where materials transport properties are sensitive to the surface and interface conditions such as surface states, surface charges, defects, traps, and dipole layers, offers a great opportunity to unravel the mechanistic basis of electronic interactions at hetero-interfaces. It can also potentially provide a nondestructive method for doping nanoscale semiconductors with molecular-scale precision. Moreover, this work will explore the possibility and develop strategies to grow highly ordered and tunable organic molecular thin films which have been proven to be a significant challenge due to the delicate balance required between the interactions governing the molecular growth, i.e., the molecule-substrate and molecule-molecule interactions. Scientifically, the aim is to promote the understanding and control of hetero-interfaces between organic and inorganic materials. Technologically, the hetero-interfaces are crucial in the development of organic electronics, molecular electronics, molecular and biological sensors, and energy converting devices.

FY 2014 HIGHLIGHTS

(1) Achieve the growth of highly ordered organic molecular thin films in both the in-plane and out-of-plane directions on the deactivated Si(111)-B surface. Recently, we reported the multilayered growth of zinc phthalocyanine (ZnPc) on the Si(111)-B surface. We find that access to the anisotropic step-flow growth mode provides a means to accomplish long-range in-plane molecular ordering. Meanwhile, the titled orientation of the ZnPc molecules allows for the out-of-plane π - π stacking, leading to the formation of a stable molecular structure with the same molecular packing to coverage of 40 monolayers. (2) Explore the effects of Ehrlich-Schwoebel barrier (ESB) and grain boundary crossing barrier on the growth dynamics of organic thin films. It is known that energetics and kinetics both play important roles in controlling the thin film morphology. In the ZnPc growth on the Si(111)-B surface, we find that the Ehrlich-Schwoebel barrier (ESB) associated with the ZnPc step edges is negligible, while the formation of molecular domain boundaries provides an activation barrier and additional nucleation sites. By increasing the substrate temperature, the grain boundary density is significantly reduced, resulting in a well-controlled surface morphology.

Giant Electrocaloric Effect in Ferroelectric Polymers with Tailored Polar-Nanostructures

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

Basic molecular and nanostructural considerations, experimental results, and phenomenological theory all suggest the existence of giant electrocaloric effect (ECE) in the normal ferroelectric and defect modified polyvinylidene fluoride (PVDF) based polymers. The research works supported by this DOE program confirmed this hypothesis and demonstrated that indeed giant ECE can be obtained in the normal ferroelectric P(VDF-TrFE) (TrFE: trifluoroethylene) copolymer and relaxor ferroelectric polymers. In the DOE program, we showed that in P(VDF-TrFE) 55/45 mol% copolymer, an isothermal entropy change $\Delta S > 50$ J/kgK and adiabatic temperature change $\Delta T > 12$ °C can be induced at ferroelectric-paraelectric transition (FE-PE). Moreover, by defects modification which converts the normal ferroelectric into a relaxor ferroelectric, we demonstrated a $\Delta T \sim 20$ °C and $\Delta S \sim 100$ J/kgK near room temperature in the high energy electron irradiated P(VDF-TrFE) 68/32 mol% copolymer. In this DOE program, a specially designed high resolution calorimeter was developed which directly measures ECE in polymer films. This new calorimeter at Penn State allows us to expand our study of ECE to ferroelectric polymers with first order FE-PE transition and to defects modified ferroelectric polymers, both of which can't be studied using the indirect method, i.e., the Maxwell relations. In this DOE program, we also showed that the defects modification in ferroelectric materials has the promise of further enhancing ECE. Proper defects modifications can significantly reduce the polar correlation and increase the number of polar entities beyond that allowed by the macroscopic symmetry of the crystal structures, both of which will result in larger entropy change between the dipolar-ordered and disordered states.

FY 2014 HIGHLIGHTS

During this time period, we systematically studied nanocomposite EC materials. One objective of this study is to answer the question of how to significantly improve the EC response at low electric field in the relaxor polymer in particular and in square law dielectrics in general by material synthesis. Here we synthesized a class of novel nanocomposites which establish a built-in material DC bias field in the relaxor ferroelectric polymers, and consequently to significantly improve EC response at low electric fields. We show that in a polymer blend (nanocomposite) with a properly controlled normal ferroelectric in nano-phase dispersion in the relaxor polymer matrix, the charge neutrality in the blends can generate an internal biasing field, leading to more than 40% enhancement in the ECE at low electric field. Inorganic/organic nanocomposites, due to the large interfacial areas and large contrast in many material properties, provide an ideal material system to study ECE and to probe synthesis approaches to markedly enhance the ECE. Here, we investigate nano-composites with inorganic ferroelectric nanofillers, which possess much higher dielectric constant than that of the polymer, and BN nano-sheets, which possess high thermal conductivity (> 500 W/mK) as an highly insulation material, to study how the ECE and thermal conductivity can be tailored and enhanced. Experimental results indicate that these ferroelectric nanofillers, through interfacial effect, can lead to significant enhancement of ECE (more than 100% enhancement) in the nanocomposites. Furthermore, by incorporating small vol% of BN nano-sheets, both the thermal conductivity and the dielectric strength are improved. This material system opens up a totally new avenue of developing EC materials and provides an interesting material system to developing scientific understanding on the multiferroic effects and interfacial effects.

In Situ Visualization and Theoretical Modeling of Early Stages of Oxidation of Metals and Alloys

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Funding: \$150,000 (2014)

PROGRAM SCOPE

Acquiring the ability to manipulate the microscopic processes governing the surface oxidation via either controlling the reaction environment or modifying the materials has huge technological implications. The work proposed therefore encompasses an atomic-scale study of the reaction ranging from the initial stage of oxygen surface chemisorption to the subsequent stages of nucleation and growth of bulk oxide. These studies exploit the unique in-situ capabilities of microscopy and spectroscopy techniques to dynamically measure the surface structure and surface chemistry of Cu, Cu-Au, and NiAl alloys under a wide range of oxidation conditions. Three research goals are pursued through this program: 1) Tune oxygen chemisorption induced surface phase transitions via oxygen pressure and temperature; 2) Tune the crossover from on-surface oxygen chemisorption to subsurface oxygen incorporation; 3) Tailor the growth morphologies of oxide nanoislands via metal/oxide interfacial strain. The in-situ experiments are coordinated closely by a number of theoretical modeling techniques ranging from the first-principles calculations to continuum elastic theory for developing direct insight into the reaction mechanism, including adsorption sites, diffusion path, reaction barrier, and surface/interface effects. The study allows for identifying how the interplay between thermodynamics and kinetics determines the final structure, composition, and oxidation mechanism, and also provides the baseline for tailoring the structures and composition of materials to steer the reaction toward the desired direction.

FY 2014 HIGHLIGHTS

A detailed understanding of the initial oxidation processes of surfaces has always been complicated by overwhelming inhomogeneities due to high density of defects. Atomic steps are present on virtually any crystalline material in any environment and serve as natural sources and sinks of substrate atoms owing to the reduced coordination of atoms at step sites. Through the use of a combination of *in situ* microscopy tools and theoretical modeling, we have addressed several outstanding issues in oxidation induced surface dynamics as a result of mass transfer from and to steps: 1) Using *in situ* STM, we were able to follow the nucleation and growth of -Cu-O- added-row reconstruction with the coordinated retraction of surface steps of the Cu(110) substrate, which provides direct evidence that surface steps are the source of Cu adatoms for the Cu(110)-(2x1)-O restructuring. 2) Using *in situ* aberration-corrected environmental TEM, we visualized oxide film growth at atomic resolution during the oxidation of stepped Cu surfaces. We observed that the presence of surface steps leads to the decomposition of the oxide overlayer at the growth front, thereby resulting in oscillatory oxide film growth that proceeds in tandem with the propagation of the surface step. 3) Using in-situ low-energy electron microscopy (LEEM) that spatially and temporally resolves oxide film growth during the oxidation of NiAl(100), we demonstrated that surface steps are impermeable to oxide film growth. The advancement of the oxide occurs exclusively on the same terrace and requires the coordinated migration of surface steps. The

resulting piling up of surface steps ahead of the oxide growth front progressively impedes the oxide growth.

DOE National Laboratories

Molecular Beam Epitaxy of Superconducting Oxides

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Funding: \$1,284,000 (2014)

PROGRAM SCOPE

The mechanism of high-temperature superconductivity (HTS) is arguably still the most important open problem in Condensed Matter Physics. Some of the most basic questions - what is the role of dimensionality in the HTS phenomenon, what are the spin and the charge of free carriers, what is the nature of superconducting transition, and what is the 'glue' (boson excitations) responsible for electron pairing - are still being debated. The research project relies on a unique molecular beam epitaxy (MBE) system for atomic-layer ('digital') synthesis of complex oxides. We fabricate single-crystal films of various cuprates and other complex oxides (nickelates, bismuthates, etc.), as well as multilayers and superlattices with atomically perfect interfaces. We manufacture heterostructures as well as HTS nanowires, nanorings and nanodots, and perform on them a series of experiments – some in-house and others in collaboration with leading experimental groups elsewhere – that were not previously possible. These experiments are aimed at providing conclusive answers to at least some of the above questions, and significantly impact research on HTS and more broadly on strongly-correlated materials. Correlated electron materials, transition-metal oxides, and HTS in particular are the main thrust of research at CMPMS Department and BES Directorate at BNL. Atomic-layer-by-layer MBE technique to synthesize perfect films and interfaces and to exploit epitaxial effects, and the identification of essential interactions giving rise to HTS, have been singled out as a Priority Research Direction in the latest BES Workshop on Superconductivity.

FY 2014 HIGHLIGHTS

The MBE laboratory, including a clean room, is fully functional at the peak performance. In FY 2014 we have performed over 200 synthesis experiments, most of which produced atomically smooth superconducting films. Every film was characterized by reflection high-energy electron diffraction (RHEED), atomic force microscopy (AFM), and transport and/or mutual inductance measurements, and selected ones also by x-ray diffraction (XRD). Many were patterned into micro- or nano-sized devices and were subject to detailed study of their physical properties and behavior, resulting in a number of new observations and results. These were reported in nine journal papers published in FY 2014, including two in Nature Materials and one in Nature Nanotechnology; one more was accepted for publication in Nature Physics (where it was published in December 2014). FY 2014 Recognition, Honors, and Awards: I. Bozovic was elected to the Academia Europea (the European Academy of Humanities, Letters and Sciences) in recognition of his lifetime achievements. He is a Foreign (Honorary) Member of

the Serbian National Academy of Sciences, Fellow of APS and SPIE, and a Member of the Editorial Board of Journal of Superconductivity, Journal of Nanophysics Letters, and ISRN Condensed Matter Physics. He won the prestigious award for Materials Synthesis from the Gordon and Betty Moore Foundation, one of only twelve that have been awarded nationwide and the only one awarded to a full-time employee of a National Laboratory. He was also elected an Adjunct Professor in the Applied Physics Department, Yale University. In FY 2014, he has been a Chair or Member of The International Advisory Boards of 10 international conferences. He received 22 official invitations to give invited talks at international conferences in FY 2014. Two invited talks were given by A. T. Bollinger and J. Wu, respectively.

Electronic, Magnetic and Optical Properties of Doped Metal Oxide Epitaxial Films and interfaces

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Funding: \$879,000 (2014)

PROGRAM SCOPE

We explore fundamental phenomena related to electron-hole pair creation, propagation, and lifetime, collective defect interaction, and carrier spin polarization in complex oxide epitaxial films, heterojunctions and superlattices. Understanding these phenomena paves the way for effective and scientifically informed use of oxides in photovoltaics, photo- and thermo-electrochemical, and spintronic device technologies. These materials are synthesized with state-of-the-art control and purity for the purpose of understanding the intricate relationships that exist between composition, structure and functional properties using molecular beam epitaxy in conjunction with a state-of-the-art atom beam flux monitoring technology developed in this program. The resulting material systems are characterized using a variety of methods aimed at accurately determining composition, global and local structure and the kinds and quantities of defects present. Electronic, optical, magnetic and magnetoelectronic properties are measured and interpreted in light of realistic, as opposed to idealized, models of the material system. Deep insight is gained by coupling experiment with classical and quantum mechanical modeling efforts. A key goal is an in-depth understanding of not only how defects influence properties, but also how defects can be harnessed and controlled for useful purposes. The specific scientific themes being investigated include: (i) tailoring electronic and optical properties through alloying, superlattice formation, and strain for the purpose of efficient visible light harvesting, (ii) exploring collective defect phenomena to generate novel and useful mesoscale structures, and, (iii) using ferromagnetic complex oxides for spin injection into non-magnetic semiconductors in simple spintronic devices.

FY 2014 HIGHLIGHTS

We discovered that the semiconducting phase, SrCrO_{2.8} (R-SCO), contains planes of ordered oxygen vacancies which allow O²⁻ to rapidly diffuse through the material at low temperature, a property of considerable importance in solid oxide fuel cells. These O-deficient planes act as fast diffusion paths for O anions, leading to relatively low-temperature (~250°C) in-air oxidation of R-SCO to SrCrO_{3.6} (P-SCO).

Fast O^{2-} diffusion at low temperature is highly desirable for solid oxide fuel cells in that the overall efficiency of the cell is greatly enhanced by being able to diffuse O^{2-} through the cathode at low temperature, whereas $\sim 800^\circ\text{C}$ is required with materials currently in use. Through the use of *ab initio* modeling, we were able to gain mechanistic understanding of O^{2-} diffusion in R-SCO, leading to the low-temperature oxidation of R-SCO to P-SCO. We have investigated the evolution of the structural and electronic properties of $\text{La}_{1-x}\text{Sr}_x\text{CrO}_3$ ($0 \leq x \leq 1$) epitaxial films deposited by molecular beam epitaxy. LaCrO_3 is an antiferromagnetic insulator whereas SrCrO_3 is a metal. Substituting Sr^{2+} for La^{3+} in LaCrO_3 effectively dopes holes into the top of valence band, leading to Cr^{4+} ($3d^2$) local electron configurations. Core-level and valence-band features monotonically shift to lower binding energy with increasing x , indicating downward movement of the Fermi level toward the valence band maximum. The material becomes a p-type semiconductor at lower doping levels and an insulator-to-metal transition is observed at $x \geq 0.65$. Valence band x-ray photoemission spectroscopy reveals diminution of electronic state density at the Cr $3d$ t_{2g} -derived top of the valence band while O K-edge x-ray absorption spectroscopy shows the development of a new unoccupied state above the Fermi level as holes are doped into LaCrO_3 . These results indicate a pronounced redistribution of electronic density of states upon hole doping, a result that is also obtained by density functional theory with a Hubbard U correction.

EARLY CAREER: In-Situ Monitoring of Dynamic Phenomena During Solidification

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Funding: \$500,000 (2014)

PROGRAM SCOPE

Solidification is experienced by all metals and is critical to the manufacture of components, from cast aluminum alloy engine blocks to the growth of single crystal superalloy turbine blades. Solidification is multiscale, ranging from the microscopic scale, where solid-liquid interface stability dictates solidification pattern and structural development, to the macroscopic scale, where casting mold filling, intended heat-transfer, and solidification progression are crucial. We experimentally visualize the dynamics of controlled metal solidification from the microscopic to the macroscopic scale by imaging with electrons, x-rays, and protons. Our movies are used to inform and develop multiscale computational models of metal solidification, enabling predictive capability. We have performed x-ray imaging of controlled growth and microscopic structural development in aluminum-copper alloys during solidification and the first quantitative phase-field simulation comparison, proton imaging of casting mold filling at the macroscopic scale and modeling informed by experiments, and dynamic transmission electron microscopy of nanocrystalline aluminum-silicon alloy films to study rapid solidification relevant for processes such as additive manufacturing. We are also pursuing three-dimensional visualization of morphologically complex solidification structures and complementary experiments and modeling of the properties and performance of solidification structures. Experimental and computational visualization of solidification, coupled with controlled processing, will result in the development and deployment of manufacturing technologies for creating advanced metals with designed structures, properties, and performance.

FY 2014 HIGHLIGHTS

- The first quantitative phase-field simulation comparison with x-ray imaging of metal alloy microstructural evolution during solidification.
- X-ray imaging of metal alloys during controlled solidification at the Advanced Photon Source at Argonne National Laboratory, November 2013 and August 2014
- Casting mold filling modeling informed by proton imaging experiments.
- Proton imaging of casting mold filling with pRad (proton radiography) at the Los Alamos Neutron Science Center (LANSCE) at Los Alamos National Laboratory, October 2013 and November 2014
- Dynamic transmission electron microscopy of metal alloys during rapid solidification at Lawrence Livermore National Laboratory, July 2014
- “Controlled grain boundary grooving experiments toward fundamental understanding of hot tearing in metal alloys”, Advanced Photon Source Argonne National Laboratory, awarded 36 (8 hr) shifts, 2014-2016
- “Multiscale prediction and control of metallic alloys during solidification”, Proton Radiography (pRad) LANL, awarded 1 week of beamtime, November 2014.

Growth Mechanisms and Controlled Synthesis of Nanomaterials

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Funding: \$1,031,000 (2014)

PROGRAM SCOPE

The goal of the research program is to understand the link between the growth mechanisms and the resulting structure of nanoscale materials. The development of real-time, *in situ* methods to probe and induce chemical and physical transformations away from thermodynamic equilibrium is emphasized in order to controllably synthesize nanomaterials with metastable structures and enhanced properties. The approach relies on correlating the real-time diagnostic measurements with predictive theoretical methods and characterization by imaging, spectroscopy, and atomic-resolution analytical electron microscopy. Specific aims of the program are: (1) To understand the special role of nonequilibrium growth environments in the capture of metastable structures with novel nanoscale properties through the development of new synthesis and processing approaches incorporating *in situ* diagnostics. (2) To reveal the kinetic pathways and ultrasmall “building blocks” involved in the growth of nanostructures through the development of real-time measurement techniques. (3) To understand the atomistic interactions governing the design and synthesis of nanostructures with specific configurations and functionalities through predictive theory and associated experiments. Key synthesis and processing science challenges are addressed for major nanomaterials classes that are important to DOE's energy mission. Novel two dimensional materials (e.g., monolayers or few-layers of graphene, metal chalcogenides) are of key interest because alone or stacked into heterostructures, quantum confinement and interfacial interactions in these materials results in a wide range of emergent electronic, optical, and thermal phenomena quite different than their bulk counterparts. In addition, the hierarchical assembly of novel oxide, metal, and carbon nanoparticle architectures are of key interest for catalytic, photocatalytic and photovoltaic applications where interfacial phenomena can drive new functionality.

FY 2014 HIGHLIGHTS

Time-resolved *in situ* spectroscopy and imaging diagnostics of two-dimensional material growth processes were developed to measure the nucleation and growth kinetics of graphene, and develop models that allow its predictable synthesis. Graphene growth by chemical vapor deposition (CVD) on nickel revealed the competition between isothermal surface- and bulk-nucleation and growth, while growth on copper revealed the crucial role of suppressing nucleation and cooperative island growth to enable the synthesis of large-area (mm-scale) single-crystal graphene grains that are essential for emerging applications. Novel synthesis and processing methods were explored to synthesize 2D metal chalcogenide (2DMC) monolayers, few layers, and nanosheets (e.g., GaSe, MoSe₂, WS₂, WSe₂). The first use of pulsed laser deposition (PLD) to synthesize crystalline 2DMC nanosheets revealed how ultrasmall, stoichiometric GaSe or MoSe₂ nanoparticles form and serve as “building blocks”. A new “digital transfer growth” technique utilized these PLD-deposited ultrasmall nanoparticles as precursors, evaporated and confined between two plates to overcome boundary layer effects found in CVD, and allow the patterned growth of large 2D crystals. Finally, atomistic energetics of monolayer 2DMC epitaxial growth and subsequent layer homoepitaxy were understood through the epitaxial growth and computational modeling of GaSe monolayer crystals on graphene suspended on TEM grids. Controlled synthesis and PLD of ultrasmall TiO₂ nanoparticles was studied by *in situ* diagnostics and atomic-resolution electron microscopy to understand how these ‘amorphous’ “building blocks” assemble to form novel mesoporous architectures of nanoparticles, nanorods, and thin films with interesting metastable phases such as TiO₂ (B) at different temperatures. The synthesis and directed deposition of metal nanoparticles by femtosecond ablation of ultrathin films was also understood through experiment and computational modeling.

Structure and Dynamics in Condensed Systems

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Funding: \$2,132,000 (2014)

PROGRAM SCOPE

The research project entails bringing simulation methods together with theory and critical experiments to investigate structural selection dynamics in highly driven systems. Building on our past efforts aimed at understanding the structure and properties of highly undercooled liquids and glasses, the structural dynamics of solidification and devitrification, and the fundamental behavior of interfaces, we are developing a research program that is focused on the multi-scale structural dynamics of metallic liquids,

glasses, and crystalline phases under far-from-equilibrium conditions. By exploring this realm of material dynamics in earnest, we aim to open vast untapped domains of materials structures and physical behaviors, with an equally broad scope of potential functionality in magnetic, electric, elastic, thermal, and optical properties, and the critical coupled-response behaviors that may be strongly influenced by using far-from-equilibrium conditions to influence phase selection, crystallographic orientation, polycrystalline scale and texture, multiphase architectures, interface structure, solute distribution, and defect concentrations.

FY 2014 HIGHLIGHTS

We continued efforts in the past year to adapt the Adaptive Genetic Algorithm in collaboration with “Exploratory Development of Theoretical Methods” FWP to solve, in concert with advanced diffraction methods, the atomic structure of experimentally identified metastable phases. In FY 2013 we worked out the framework for the algorithm and began to identify previously unsolved nanoscale phases. In FY 2014 we have begun to routinely solve a number of metastable complex crystals which formed during the devitrification process in the Al-Sm system. The efficient genetic algorithm can simultaneously search a wide range of compositions for unknown crystalline phases while comparing the diffraction patterns of the calculated compounds to the experimental data.

Structural Origins of Electrochemical and Mechanical Properties in Pre-Formed Solid Electrolyte Interphases

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Funding: \$631,000 (2014)

PROGRAM SCOPE

The conduction of ions in solids and at interfaces is the key phenomenon for electrochemical energy storage and conversion. This program derives a thorough understanding of the transport of ions through concerted efforts of advanced synthesis, analytical microscopy, and neutron scattering. The goal of this project is to correlate the electrochemical and mechanical properties of solid electrolytes and solid electrolyte interphases (SEIs) to their atomic, nanoscale, and dynamic structures. The project focuses on two structurally distinct material systems: (1) crystalline oxides and sulfides, and (2) amorphous lithium phosphorous oxynitride (Lipon). New solid electrolytes have been designed based on crystalline oxide and sulfide materials. The research identifies the conduction mechanisms of solid electrolytes. The knowledge of the conduction mechanism guides the material discoveries of solid ion conductors with tailored electrochemical and mechanical properties for energy storage. Amorphous Lipon is the basis of pre-formed SEIs for high-energy batteries. Thin films of Lipon have been deposited in model battery systems to understand the function of a pre-formed SEI in conventional batteries that use liquid electrolytes. The Lipon thin film electrolyte has also been used to investigate the transport phenomenon of the all-solid state batteries that hold the promise of the next generation of high-energy, safe batteries.

FY 2014 HIGHLIGHTS

In FY 2014 this project focused on the development of solid electrolytes and pre-formed SEIs. The accomplishments can be classified as follows: (1) Implemented the concept of pre-formed SEIs to achieve excellent cyclability of high voltage batteries and high capacity batteries using conventional liquid electrolytes. In these systems, a thin film of Lipon has been deposited as a pre-formed SEI. (2) Established the new concept of bifunctional electrolyte to extend the energy storage capacity of Li-CF_x primary batteries. The solid electrolyte Li₃PS₄ was discovered as a cathode material that can be activated through a catalytic process. (3) Advanced the understanding of the structure-properties relationship of solid electrolytes. The Hard and Soft (Lewis) Acids and Bases theory was used to mitigate the air sensitivity issues of sulfide-based solid electrolytes. The space-charge effect was found to enhance the conductivity of composite electrolytes of sulfides and oxides. Aliovalent substitution was used as the approach for probing the structural dependence of ion conduction in sulfide-based solid electrolytes. The origin of grain boundary resistance of perovskite Li-ion-conducting solid electrolytes was revealed through high-resolution transmission electron microscopy. (4) We developed an *in situ* neutron scattering method for the direct observation of the phase evolution of (La_{0.8}Sr_{0.2})_{0.95}MnO_(3-δ)(LSM) and (Y₂O₃)_x(ZrO₂)_(1-x) (xYSZ, x = 3, 6, 8 and 10) for oxide conducting system.

Molecularly Organized Nanostructural Materials

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Funding: \$631,000 (2014)

PROGRAM SCOPE

Self-assembled materials with controlled nanostructures and functions have great potential for energy storage and conversion. Although many different approaches have been reported, there is a fundamental gap in the understanding of the underlining principles, in particular, the understanding and control of competing driving forces for crystal growth and three-dimensional self-assembly. The overall goal of this project is to investigate molecularly-directed crystallization and self-assembly phenomena at the interfaces for synthesizing nanostructured materials with controlled micro- and nanoporosity, desired stable crystalline phases, and tailored multicomponent three-dimensional architectures. The project focuses on well-defined experimental systems, such as two-dimensional graphene building blocks, and explores the surface chemistry in order to develop new approaches to assemble complex materials using nanoscale building blocks. The project places a strong emphasis on extensive molecular and mesoscale computer modeling to elucidate fundamental mechanisms of interfacial binding, nucleation and self-assembly and guide materials synthesis efforts. Innovative *in situ* transmission electron microscopy techniques will also be developed to obtain real-time kinetic information of nucleation, crystal growth and structural evolution. The electron and ion transport properties are measured by both microscopic and molecular spectroscopic methods, and correlated with the structure and surface chemistry of the materials. A multiscale model combining density functional theory and phase-field theory will be used to understand the coupling between resident charge transport

properties and the attendant structure-property relationships. The research consists of four subtasks: 1. Molecular interactions at the interfaces 2. Fundamentals of nucleation and growth 3. Three-dimensional assembly of functional materials 4. Charge transport and structure-property relationships.

FY 2014 HIGHLIGHTS

The project focused on the understanding of surface defects. A fluorination process is developed to semi-quantitatively probe the defects and functional groups on graphene surface (ChemSsuChem 2014). The fluorine content was modulated to investigate the different functional groups such as C-F, CF₂, O-CF₂ and (C=O)F during the fluorination process. The results of the Density function theory (DFT) and nuclear magnetic resonance (NMR) studies show that the lattice vacancies, without oxygen containing groups, provide most of the reactive sites to react with F. Functionalized graphene sheets (FGS) also contain COOH, hydroxyl or epoxy groups that contribute to the reaction products with a higher F content. We also studied hard carbon surface chemistry and solid electrolyte interphase (SEI) formation for Na ion storage (Advanced Materials, 2014). The SEI formation in Na ion chemistry is similar to that observed in more familiar Li ion systems. Electrolyte additives significantly suppress the SEI formation. Proper design of carbon surface helps other energy storage mechanisms. For example, lithium-sulfur (Li-S) batteries have recently attracted wide attention due to the high gravimetric energy density. Continuous dissolution and capacity fading during cycling remains a large challenge. A new design was developed using graphite in a hybrid anode to control undesirable surface reactions on the anode (Nature Comm. 2014). The lithiated graphite placed in front of the lithium metal functions as an active solid electrolyte interface (SEI) layer to control the electrochemical reaction while minimizing the deleterious side reactions on the surface and bulk lithium metal. Excellent electrochemical performance has been observed. Many other nanostructured electrode materials have been developed including Bi nanotubes as anode for high capacity Mg ion storage (Nano Letters 2014) and stable cathode materials (Chem. Mat., 2014).

Novel Materials Preparation and Processing Methodologies

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Funding: \$1,583,000 (2014)

PROGRAM SCOPE

The growth, control and modification of novel materials in single crystal and polycrystalline form, represent a national core competency that is essential for scientific advancement within and across traditional disciplinary boundaries, and are critical components of the Basic Energy Sciences' mission. In support of this mission, the Novel Materials Preparation and Processing Methodologies FWP focuses on developing synthesis protocols for energy-relevant materials that contain volatile, reactive or toxic components such as the rare earth (RE) metals, Mg-based and RE containing thermoelectric alloys and

Fe-As based superconductors. The objective of Novel Materials is to advance the ability to synthesize and characterize high purity, high quality materials, primarily in single crystal form; to quantify and control processing-structure-property relationships between chemical inhomogeneities and structural defects and functionality of highly responsive materials; to develop unique capabilities and processing knowledge in the preparation, purification, and fabrication of metallic elements and alloys. Single crystals are often required to achieve scientific understanding of the origin of various phenomena, whether from intrinsic or extrinsic origins, to elucidate its properties as well as to evaluate a material's full functionality.

FY 2014 HIGHLIGHTS

We developed an inverted-temperature-gradient method to grow large and high-quality single crystals of $Ba_{1-x}K_xFe_2As_2$. When setting the upper zone as the cold zone, upon cooling the nucleation initiates from the surface layer of the liquid melt. The crystallization, proceeding from the top of a liquid melt, helps to expel impurity phases during crystal growth compared to the growth inside the flux. High vapor pressure of K and As elements at the soaking temperature is also an important factor in the growth of single crystals of $Ba_{1-x}K_xFe_2As_2$. By allowing crystallization of the free surface first, evaporative losses are minimized eliminating large macro-segregation along the crystal and ensuring control of target compositions. High soaking temperature, fast cooling rate, and an adjusted temperature window of the growth are necessary to obtain single crystals of heavily K-doped crystals ($0.65 < x < 0.92$) with a sharp transition. In the efforts on studying solidification behaviors and phase space of potential thermoelectric materials made of earth-abundant and non-toxic elements, Mg-Si based materials have been selected. The phase space of pseudo binary Mg_2Si - Mg_2Sn system has been elucidated. A method to prepare single crystalline diffusion couples of air-sensitive materials by hot-pressing has been established. Utilizing the high pressure Bridgman furnace we have for the first time synthesized single crystals of Zn-bearing Fe-Ga alloys. We have grown bcc Fe-Ga-Zn single crystals up to 4.6% Zn in a Bridgman furnace under elevated pressure (15 Bar) in order to overcome the high vapor pressure of Zn and obtain homogeneous crystals. Single-crystal measurements of magnetostriction and elastic constants allow for the direct comparison of the magnetoelastic coupling constants of Fe-Ga-Zn with other magnetoelastic alloys. The partial substitution of Ga with Zn yields comparable values for the magnetoelastic coupling factor, $-b_1$, to those of the binary Fe-Ga alloys.

Exploratory Materials Synthesis and Characterization

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Funding: \$569,000 (2014)

PROGRAM SCOPE

The Exploratory Materials Synthesis and Characterization (EMSC) program concentrates on exploratory synthesis and characterization of the new model materials of current interest in condensed matter physics. In addition, we often focus on advanced synthesis of known materials in order to enable important physical and structural investigations. In our focus are correlated electron systems in energy related materials. Most often materials are synthesized in the single crystal form since many

observables of interest are tensor quantities and since this allows for the investigation of physical properties that are free of grain boundary influences. We use a range of techniques suitable for exploratory synthesis: arc melting and solid state reactions, solution methods, high temperature intermetallic, oxide, chalcogenide or salt fluxes, chemical vapor transport and deposition. Automated physical and structural characterization is the essential component of the lab. Quite often the same methods are used to probe and perturb crystal structure, transport, thermodynamic and magnetic properties, sometimes at the extreme conditions. We are regular users of NHMFL Tallahassee and HZDR Dresden. We also use EXAFS beamlines at NSLS and we are constantly engaged in the buildup of our synthesis and characterization capabilities. We currently pursue several interpenetrating directions: Quantum criticality in heavy fermions and charge density wave materials, Metal – Insulator transitions (MIT) in nearly magnetic materials, Dirac states in bulk crystals and facility development. This program includes training of the next generation of scientists. Students from neighboring universities (Brown, Columbia, Johns Hopkins, and Stony Brook) were or are being educated in materials physics, arts and crafts of crystal growth, materials synthesis and characterization.

FY 2014 HIGHLIGHTS

(1) Exploratory synthesis and characterization of novel materials. We reported electrical and thermal transport properties of the BaMn_2Bi_2 crystals. The resistivity of the antiferromagnetic BaMn_2Bi_2 shows a metal-semiconductor (insulator) transition at 80K with decreasing temperature. Correspondingly, the thermopower S shows a peak at the same temperature, approaching $150 \mu\text{V/K}$. With increasing temperature, S decreases to about $125 \mu\text{V/K}$ at the room temperature but the magnetic field enhances the peak value to $210 \mu\text{V/K}$. The Hall resistivity reveals an abrupt change of the carrier density close to the metal-semiconductor transition temperature. The origin of high Seebeck coefficient is in the sharp change in the carrier density and the metal-semiconductor (insulator) transition which is related the strongly correlated effect. Kefeng Wang and C. Petrovic, Appl. Phys. Lett. 103, 192104 (2) Advanced materials synthesis and crystal growth. Crystals made at EMSC BNL enabled imaging Cooper pairing of heavy fermions in CeCoIn_5 ; collaboration with Seamus Davis (BNL) and Dirk Morr groups (University of Illinois). The results provided direct evidence for a magnetic f-electron-mediated Cooper pairing mechanism of heavy-fermion superconductivity in CeCoIn_5 . It should be noted that many other important experimental results from diverse techniques were explained within this framework. J. S. Van Dyke, F. Massee, M. P. Allan, J. C. Seamus Davis, C. Petrovic and D. Morr, Proc. Natl. Acad. Sci. U. S. A. 32, 11663 (2014).

Fundamental Studies of Synthesis of Nanomaterials: A Joint Challenge for Plasma and Materials Science

Institution: Princeton Plasma Physics Laboratory
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Principal Investigator: Yevgeny Raitses
Sr. Investigator(s): Igor Kaganovich; Princeton Plasma Physics Laboratory
Brent Stratton; Princeton Plasma Physics Laboratory
Roberto Car; Princeton University
Bruce Koel; Princeton University
Predrag Krstic; Theoretik, LLC
Mikhail Shneider; Princeton University
Mohan Sankaran; Case Western Reserve University
Michael Keidar; George Washington University
Students: 3 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)

Funding: \$1,300,000 (2014)

PROGRAM SCOPE

This research project explores the fundamental physics of nanomaterial synthesis by plasma with the goals to understand, predict, and ultimately control the synthesis processes, including plasma generation and nucleation and growth of nanoparticles and nanostructures. The research focuses on three key areas: (1) characterization of the plasma properties relevant to synthesis of nanomaterials; (2) development and utilization of in-situ diagnostics of nanoparticles and nanostructures; and (3) understanding plasma-mediated synthesis for various nanomaterials, including development, validation, and integration of codes for multiscale modeling of nanomaterial synthesis. The emphasis is on carbon, boron nitride, and hybrid B-C-N nanostructures. A comprehensive set of in-situ plasma and nanoparticle diagnostics will be developed and employed to provide the dataset needed to validate and further develop theoretical models of plasma and nanostructure growth.

FY 2014 HIGHLIGHTS

This project was funded in August 1, 2014. Since then, we made a good progress in terms of initiation and coordination of research efforts in three main research directions, including modeling, diagnostic development and plasma synthesis experiments. In particular, we initiated characterization of electrode evaporation-deposition processes in the carbon arc using weighting procedures and applying optical emission spectroscopy, high speed imaging and IR imaging, segmented electrodes. On the diagnostic development, we are completing designs of the proposed *in situ* laser diagnostics of nanoparticles. In support of these efforts, we are working on modeling of laser-induced effects on nanoparticles in the presence of the plasma. Candidates for the two diagnostic and one theory post doc positions were interviewed. The selected candidates were recently hired.

Surface Structures Far-From-Equilibrium

Institution: Ames Laboratory
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Sr. Investigator(s): Kai-Ming Ho; Ames Laboratory
Pat Thiel; Ames Laboratory
Cai-Zhuang Wang; Ames Laboratory
Students: 0 Postdoctoral Fellow(s), 3 Graduate(s), 0 Undergraduate(s)
Funding: \$561,000 (2014)

PROGRAM SCOPE

The emergence of novel properties in nanostructures can be related to various factors, important ones being electron confinement and lower atom coordination. The goals of this FWP are two-fold, first to grow epitaxially controllable nanostructures and second to use their novel, selectable properties on several technologically important problems. Achieving these goals it is also essential to find ways to tune atomistic processes (diffusion, adsorption) and use them to grow perfect nanoscale patterns easily and in short times. Such studies have been carried out in several specific systems. Understanding metal growth on graphene, graphite and other carbon coated substrates is one of the areas of interest because graphene based devices require stable metal contacts of low electrical resistance. Novel

graphene properties can emerge after metal intercalation. Robust ways were found to speed up adatom diffusion, from the electric field generated in regions of different workfunction on metal islands or when 2-dimensional metallic overlayers become extremely mobile after compressed to densities higher than their crystalline densities. Understanding the growth mechanism for defect-free nanowires with high and tunable aspect ratios on carbon coated surfaces is relevant for magnetic and optoelectronic applications.

FY 2014 HIGHLIGHTS

In FY 2014 the team elucidated the difference in workfunction between adjacent terraces on a Pb(111) mesa grown over stepped Si surface generates a lateral electric field that changes stochastic to biased diffusion of Mg adatoms with the Mg adatoms populating terraces of low workfunction. In collaboration with two outside groups the “Devil’s Staircase” (DS) phases in Pb/Si(111) were used to test how robust is 1-layer superconductivity using high resolution spectroscopy with millikelvin STM and to show very fast pattern formation between the DS phases at low temperature after deposition of C₆₀ fullerenes.

Theoretical Condensed Matter Physics

Institutions Receiving Grants

Theory of Computation for Semiconductor Catalysis of Solar Water Splitting

Institution: New York-Stony Brook, State University of
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Email: philip.allen@stonybrook.edu
Principal Investigator: Philip Allen
Sr. Investigator(s):
Students: 0 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding: \$140,000 (2014)

PROGRAM SCOPE

The aim is to improve theoretical understanding of processes by which solar energy can be captured at catalytic interfaces (e.g., the semiconducting GaN/water interface) to drive the reaction $2 \text{H}_2\text{O} \rightarrow 2 \text{H}_2 + \text{O}_2$. Computation (primarily density functional theory) provides the method to simulate processes and to interact with experiment. This work also trains physics graduate students working at the interface between physics and chemistry. A primary material for study is the wurtzite-structure alloy of GaN with ZnO, apparently stable over the full concentration range x of $\text{Ga}_{1-x}\text{Zn}_x\text{N}_{1-x}\text{O}_x$. The predicted bond-length relaxations and strong short-range concentration correlations are being tested experimentally. We develop theories of optical and dc conductivity of the bulk alloy. We study the structure and thermodynamics of the clean and the wet surfaces of this alloy. We ask how alloying affects the photo-absorption spectrum and carrier mobility. We study bulk and surface carrier traps and their importance for photo-catalysis. We are generalizing the USPEX (Universal Structure Predictor: Evolutionary Xtallography) genetic structure-predicting algorithms in order to predict thermodynamically relevant surface and interface structures. We study the perovskite-structure polar materials of the $\text{CaTiO}_3/\text{SrTiO}_3/\text{BaTiO}_3$ family. Their interfaces with water offer new ways to tune the photochemistry.

FY 2014 HIGHLIGHTS

Progress is occurring on four projects. (1) The clean non-polar (10-10) surface of GaN in contact with water is an important model system for surface chemistry. The first monolayer of water largely splits into Ga-OH and N-H surface species. The reactivity of these species when GaN is photo-excited is being studied. (2) Crystal structure prediction computer codes have been modified to assist in surface structure prediction. A surprising new candidate structure of the polar (0001) surface of ZnO in the presence of hydrogen is predicted. (3) Atom relaxation of large supercells representing characteristic configurations of GaN/ZnO alloys has been simplified. This enables “pre-relaxed” configurations to initiate the final expensive density-functional relaxation. (4) The oxidation of water on the SrTiO_3 (100) surface has been quantified.

Electron Interaction Effects in Nanosystems

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Principal Investigator: Anton Andreev

Sr. Investigator(s):

Students: 0 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)

Funding: \$150,000 (2014)

PROGRAM SCOPE

The research program aims to develop a theory of electron transport in nanosystems with strongly correlated carriers. The work is organized around the following themes. (i) Theory of electron transport beyond the Fermi- and Luttinger- liquid paradigms. Charge carriers in high mobility semiconductor nanostructures often form strongly correlated liquids in which the energy of Coulomb repulsion U exceeds the Fermi energy, ϵ_F . In this case there is a wide and largely unexplored interval of temperatures, $\epsilon_F < T < U$, in which the Fermi-liquid (or Luttinger liquid in one-dimension) description is inapplicable but the liquid remains strongly correlated. Part of the research program focuses on development of a theory of electron transport in one- and two- dimensional high mobility systems in the regime where the Luttinger- or Fermi- liquid description becomes insufficient or inadequate. This work will advance our understanding of electron transport in semiconductor nanostructures with strong Coulomb repulsion between the charge carriers. (ii) Transport phenomena in non-centrosymmetric media. Another part of the research program aims to develop theory of transport phenomena in non-centrosymmetric (and/or time reversal non-invariant) conductors and superconductors. This includes 1) theory of linear and circular photogalvanic effect and the Kerr effects in chiral magnets and superconductors, 2) photogalvanic effect in monolayers of transition metal dichalcogenides, and 3) theory of spin and charge transport in normal metal/p-wave superconductor structures with the chiral $p_x + ip_y$ symmetry of the order parameter.

FY 2014 HIGHLIGHTS

(1) Equilibration of spin-degenerate one-dimensional electron liquid in the Wigner crystal regime: We developed a theory of equilibration of one-dimensional electron liquids at strong interactions, Phys. Rev. B 90, 035148 (2014). (2) Theory of Coulomb drag (CD) in the hydrodynamic regime: We developed a theory of CD in clean double layers with strongly correlated carriers. If the equilibration length of the electron liquid is shorter than the interlayer spacing CD arises from hydrodynamic density fluctuations. We expressed CD resistivity in terms of kinetic coefficients of the electron fluid. Our results are nonperturbative in interaction strength and do not assume Fermi-liquid behavior of the electron liquid. Phys. Rev. B 89, 121104(R)(2014). (3) Theory of disordered unconventional superconductors: Unconventional superconductors are easily driven to the normal state by disorder. In the vicinity of the normal-metal-superconductor transition the superconducting state consists of superconducting islands connected by Josephson links. Kivelson and Spivak showed that for d-wave superconductors the Josephson junction model reduces to the Mattis model. We extended the theory to p-wave materials. The Mattis model is the leading approximation in the inter-island distance. We studied corrections to the Mattis model and stability of the superconducting phase with respect to perturbations to the Mattis model Hamiltonian. arXiv:1405.7090, accepted to JETP. (4) Aharonov-Bohm (AB) oscillations in singly-connected disordered conductors: We showed that AB oscillations exist even in singly-connected disordered conductors. They arise from quantum interference of a special class of diffusive electron trajectories that graze the sample boundary. The manuscript, arXiv:1412.5209, has been submitted to Phys. Rev. Lett.

Theory of Fluctuating and Critical Quantum Matter

Institution: California-Santa Barbara, University of
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Sr. Investigator(s):
Students: 0 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding: \$315,000 (2014-2016)

PROGRAM SCOPE

The project centers on the theory of phenomena in electronic materials involving strong quantum fluctuations, which arise due to frustration, exotic interactions (especially those originating from spin-orbit coupling), and proximity to quantum critical points. The projects are divided roughly into two areas: phases of frustrated quantum magnets, and quantum critical points in itinerant systems with frustrated or exotic interactions. All components are connected both to specific experiments and materials, and to general issues at the forefront of the theory of correlated quantum matter. The research will guide theory and experiment in the search for exotic highly entangled quantum phases such as quantum spin liquids and spin nematics. A microscopic understanding of frustrated Kondo lattice systems and doped iridates will be developed, and the appropriate field theories for recently discovered and newly proposed quantum critical points will be formulated. We will extend and develop methodology from model building to numerics, to field theory methods. The work will provide specific predictions for materials and experiments to observe new physics at the frontiers of condensed matter physics.

FY 2014 HIGHLIGHTS

One of the major focuses of the research supported by this grant has been on novel types of quantum criticality. We discovered an intriguing example in the pyrochlore iridates: a quantum phase transition from paramagnetism to antiferromagnetism, in the presence of nodal fermions. We showed how this transition fits naturally into the experimentally observed sequence of rare earth iridates, and is consistent with observations of magnetism and transport in these materials. We derived a universal quantum field theory description for the transition, and solved it using renormalization group methods. The results provide a singular example of a critical magnetic order parameter strongly coupled to electronic quasiparticles, for which a fully controlled theory exists. We are currently working to extend this theory to include the effects of doping, and to describe electrical transport in a more quantitative fashion. A separate effort has been to continue our study of spin-orbit liquids, including a collaboration with an experimental group in Augsburg on the optical properties of such systems. Our theory, formulated earlier under DOE support, predicted this spin orbital liquid and a proximate quantum critical point. Now we discovered some direct evidence for the criticality in optical excitations, and performed new theoretical calculations to compare with the measured spectra. Lastly, we are working on a new theory of frustrated ferromagnets, which explains how these types of materials support metamagnetism, chirality, and multipolar order. We have made considerable progress in formulating a new theory for these systems, deriving it for relevant microscopic models, and solving it in some of the most relevant limits. This effort is being aided by development of a new DMRG (Density Matrix Renormalization Group) code, which is now close to completion. We expect to report first results from these efforts in the coming year.

Electronic Structure, Spectroscopy and Correlation Effects in Novel Materials

Institution: Northeastern University
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Principal Investigator: Arun Bansil
Sr. Investigator(s): Robert Markiewicz; Northeastern University
Students: 2 Postdoctoral Fellow(s), 4 Graduate(s), 0 Undergraduate(s)
Funding: \$810,000 (2014-2016)

PROGRAM SCOPE

This project is targeted on modeling and understanding electronic structure, spectroscopies, and correlation effects in novel materials of current interest. We are pursuing techniques for realistic treatment of electronic spectra of a wide variety of materials, which serve as a prelude to formulating and implementing methodologies for making direct connection with various spectroscopies. This project is concerned specifically with, angle resolved photoemission (ARPES), resonant inelastic x-ray scattering (RIXS), scanning tunneling microscopy/spectroscopy (STM/STS), magnetic and non-magnetic Compton scattering, and positron annihilation spectroscopy related issues. Specific systems being investigated are cuprates and Fe-based superconductors, topological materials, 2D spin-orbit coupling driven thin films beyond graphene, nanocrystals, and Li-battery materials. Our goal is to exploit the strengths of various spectroscopies to piece together a complete picture of electronic states, enabling direct and sharpened confrontations with theoretical models, and help advance the reach of various spectroscopies. With current and planned high-resolution beamlines at various DOE supported facilities, tremendous amounts of data are becoming available, launching a new era for probing the huge phase space of experiments as a function of temperature, magnetic field, doping and substitutions in the normal and the superconducting state. It will be difficult to effectively utilize this powerful instrumentation without parallel theoretical efforts of the sort being pursued here to develop sophisticated modeling methodologies, including key effects of strong correlations, electron-phonon coupling, and various nanoscale heterogeneities. The proposed program will help fill this critical gap by continued development of increasingly sophisticated theoretical tools for analyzing and interpreting the most important highly resolved spectroscopies in wide current use today.

FY 2014 HIGHLIGHTS

(I) Topological Insulators (TIs): Progress made includes: (1) Analysis of scanning tunneling spectra to unveil the orbital texture of $Pb_{1-x}Sn_xSe$ topological crystalline insulator; (2) We investigated the delicate relationship between quantum tunneling and Fermi surface (FS) spin polarization in ultrathin Bi_2Se_3 films, suggesting that the polarization current can be tuned to zero in thin insulating films to provide a basis for a future spin-switch nanodevice; (3) We showed that the surface of $Sr_3Ir_2O_7$ near a metal-Mott insulator transition exhibits weak metallicity, shedding light on transport phenomena in iridate-based devices. (II) 2D atomically thin layered materials: Various 'beyond graphene' 2D materials were studied, and their potential in new devices for manipulating spins was explored in silicene/germanene nanoribbons. In considering effects of strains/substrates we showed that tensile strain can convert freestanding bilayers of group IV and V elements into TI phases, and hydrogenation has a similar effect on tin films. (III) FS reconstruction in the pseudogap state of Bi2201: We found evidence for the appearance of a FS in the antinodal region near optimal doping, far from the point of pseudogap collapse, which could also support anomalous 'FS-free superconductivity'. (IV) Core hole effects in RIXS and $S(q,\omega)$: We introduced a numerically soluble model in which electrons are noninteracting except for

a Hubbard-like attraction to a static core hole. The one-boson contribution in the resulting spectrum can be understood as $S(q,\omega)$ dressed by matrix element effects, which divide the spectrum into well- and poorly-screened components, and display a remarkable relation to the x-ray edge singularity. (V) Gutzwiller calculations of competing orders in cuprates: We investigated magnetic and charge instabilities within the Gutzwiller approximation RPA (GA+RPA), finding evidence for phonon-coupled charge density waves, and a secondary nematic order, pinned by disorder effects.

Quantum Phases in Nanosystems: Dissipation, Interactions, and Non-Equilibrium Phenomena

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Principal Investigator: Harold Baranger
Sr. Investigator(s):
Students: 0 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding: \$120,000 (2014)

PROGRAM SCOPE

This project concerns the intersection of three major themes of contemporary condensed matter physics: First, open quantum systems (a quantum system interacting with an environment) are receiving increasing attention because of processes of societal relevance such as photosynthesis and energy capture. Second, quantum simulation of strongly interacting systems is being widely pursued as a way of producing exotic states of matter. Third, non-equilibrium quantum systems are becoming more appreciated for the qualitatively new phenomena produced. This project focuses on how dissipative nanoscale systems can elucidate these three themes by making use of the amazing control that is experimentally possible. The building block in this theoretical work is a quantum dot coupled to a dissipative electromagnetic environment. Several experimental groups are pursuing this platform, including our collaborator G. Finkelstein here at Duke. We have recently shown that this system can emulate resonant tunneling in an interacting one-dimensional system, revealing a quantum phase transition. We demonstrate that it can be described by a Majorana fermion model and thereby account for the experimentally observed conductance at the quantum critical point. The plan for the present project is to further explore possibilities for producing exotic quantum states and phenomena by using quantum dots coupled to dissipative electromagnetic environments. This work contributes a thorough understanding of a well-controlled open quantum system with strong correlation effects and exotic states of matter. Such an understanding impacts the larger question of how and when such phenomena occur, and so whether they may be relevant for open quantum systems involved in energy capture. The impact of environmental dissipation on quantum behavior is a key issue for nanoscale systems, which are often at the juncture where microscopic quantum objects and macroscopic environments meet.

FY 2014 HIGHLIGHTS

Accomplishments regarding: (1) entanglement within an environment coupled to a two-level system, (2) quantum phase transitions in a dissipative resonant level. Unveiling Environmental Entanglement in Strongly Dissipative Qubits: The coupling of a qubit to a macroscopic reservoir plays a fundamental role in understanding the transition from the quantum to the classical world. Considering a harmonic environment, we use both intuitive arguments and numerical many-body quantum tomography to study the complete wavefunction for intense qubit-environment interaction. The resulting strongly-correlated many-body ground state is built from quantum superpositions of adiabatic (polaron-like) and non-

adiabatic (antipolaron-like) contributions of the environment. The emerging Schrodinger cat environmental wavefunctions are described quantitatively via simple variational coherent states. In contrast to qubit-environment entanglement, we show that entanglement among the modes in the reservoir is crucial to stabilize qubit superpositions in regimes where standard theories predict an effectively classical spin. Dissipative Resonant Level: We study tunneling through a resonant level connected to two dissipative bosonic baths: one is the resistive environment of the source and drain leads, while the second comes from coupling to potential fluctuations on a resistive gate. We show that several quantum phase transitions (QPT) occur and obtain the phase diagram. For strong dissipation, a BKT-type (Berezinsky-Kosterlitz-Thouless) QPT separates strong-coupling and weak-coupling (charge localized) phases. In the source-drain symmetric case, all relevant backscattering processes disappear at strong coupling, leading to perfect transmission at zero temperature. In fact, a QPT occurs as a function of the coupling asymmetry: the two phases are (i) the system is cut into two pieces (zero transmission), or (ii) it is a single connected piece with perfect transmission, except for a disconnected fractional degree of freedom.

Properties of Multiferroic Nanostructures from First Principles

Institution: Arkansas, University of
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Principal Investigator: Laurent Bellaiche
Sr. Investigator(s):
Students: 1 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding: \$10,000 (2014)

PROGRAM SCOPE

Objectives: This project will build a research program aimed at (1) investigating complex phenomena in multiferroic nanostructures; and (2) designing new low-dimensional multiferroic materials with optimal or original properties. Description: The research objectives will be achieved through the development and use of the following *ab initio* numerical tools: (i) accurate first-principles techniques; (ii) effective Hamiltonian approaches that extend the reach of first-principles calculations by realistically mimicking complex (static and dynamical) properties of multiferroic nanostructures at finite temperature; and (iii) the inverse method that allows an efficient design of materials with improved properties. Collaborations with internationally-known experimental groups will also be strengthened. The proposed cooperative activities will allow a careful side-by-side comparison between predictions and measurements, which is important to fully understand the systems to be investigated and to validate the numerical tools to be developed. This research program will also be integrated into the educational experiences of postdoctoral and graduate students. Many compounds and effects are going to be studied. Potential impact: A broad and deep knowledge of complex phenomena, multiferroics and nanoscience will be gained thanks to the techniques to be developed, and the variety of systems/effects to be investigated. In addition to build a network that will be the basis for future collaboration and exchange of students between the involved institutions, the collaborative efforts have also the potential to result in the realization of devices with enhanced and/or new functionalities, and that will improve energy efficiency and storage.

FY 2014 HIGHLIGHTS

Studies published within fiscal year 2014: [1] "Prediction of a novel magnetoelectric switching mechanism in multiferroics," Yurong Yang, Jorge Iniguez, Ai-Jie Mao and L. Bellaiche, *Physical Review Letters* 112, 057202 (2014). [2] "Novel magnetic arrangement and structural phase transition induced by spin-lattice coupling in multiferroics," Satadeep Bhattacharjee, Dovran Rahmedov, Laurent Bellaiche and Dawei Wang, *MRS Communication* 3, 213 (2013). [3] "Properties of Epitaxial Films Made of Relaxor Ferroelectrics," S. Prosandeev, Dawei Wang and L. Bellaiche, *Physical Review Letters* 111, 247602 (2013). [4] Ultrafast switching of the electric polarization and magnetic chirality in BiFeO₃ by an electric field," Satadeep Bhattacharjee, Dovran Rahmedov, Dawei Wang, Jorge Iniguez and L. Bellaiche, *Physical Review Letters* 112, 147601(2014). [4] "Prediction of novel interface-driven spintronic effects," S. Bhattacharjee, S. Singh, D. Wang, M. Viret and L. Bellaiche, *Journal of Physics: Condensed Matter* 26, 315008 (2014). [5] "Near room-temperature multiferroic materials with tunable ferromagnetic and electrical properties," Hong Jian Zhao, Wei Ren, Yurong Yang, Jorge Iniguez, Xiang Ming Chen and L. Bellaiche, *Nature Communications* 5, 4021 (2014). [5] "Atomistic theory of hybrid improper ferroelectricity in perovskites," Hong Jian Zhao, Jorge Iniguez, Wei Ren, Xiang Ming Chen, and L. Bellaiche, *Physical Review B* 89, 174101 (2014). [6] "Creating multiferroics with large tunable electrical polarization from paraelectric rare-earth orthoferrites," Hong Jian Zhao, Yurong Yang, Wei Ren, Ai-Jie Mao, Xiang Ming Chen, and Laurent Bellaiche, *Journal of Physics: Condensed Matter, Fast Track Communications* 26, 472201 (2014). These articles also resulted in 9 invited talks and 6 contributed talks and/or posters at national and international conferences since 11/01/2013. - Dovran Rahmedov successfully defended his PhD of Physics in 2014.

Theoretical Investigations of Nano Bio Structures

Institution: North Carolina State University
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Principal Investigator: Jerry Bernholc
Sr. Investigator(s):
Students: 0 Postdoctoral Fellow(s), 4 Graduate(s), 0 Undergraduate(s)
Funding: \$110,000 (2014)

PROGRAM SCOPE

This proposal addresses fundamental issues in nanoscale science and technology, namely the design of nanostructured materials and devices with desired, novel characteristics. The research projects will focus on several broad areas: (i) carbon nanotube-based molecular sensors, (ii) molecular self-assembly on metal surfaces, and (iii) Li ion transport and incorporation in battery structures. These projects build on the work accomplished during the prior proposal periods, which included substantial advances to real-space electronic structure methodology and investigations of (i) novel nanoelectronic devices; (ii) copper-induced misfolding in Parkinson's disease and the action of copper-containing nitride reductase, and (iii) transition rates in cis-trans isomerization of polyproline peptides. Our newly developed capabilities enable fully quantum-mechanical simulations of solvated systems through a Quantum Mechanics (QM)/approximate-QM methodology at much reduced cost, multi-terminal non-equilibrium Green's function investigations of realistic device structures, and calculations of transition rates in rare events through non-equilibrium steered molecular dynamics. Our improved real-space multigrid method is capable of simulating the dynamics of systems containing thousands of atoms on DOE's leadership-class massively parallel super-computers.

FY 2014 HIGHLIGHTS

DNA is perhaps the world's most controllable nanowire, able to be grown in a precisely defined sequence with extremely few errors. If it can be made to conduct, it would have significant potential for applications in nanoscale sensors and electronics. However, experimental measurements of DNA conductivity span a very broad range, from highly conducting to fully insulating. We use *ab initio* techniques combined with molecular dynamics simulations to investigate B-DNA connected to carbon nanotubes via alkane linkers. The fully solvated system contains up to 78,000 atoms and is equilibrated at room temperature using molecular mechanics. For each system, 20 representative snapshots, containing up to 1,800 atoms, are extracted for quantum transport calculations. The quantum calculations include the DNA, the linkers, the first solvation shell with counterions, and the nanotube electrodes. We show that: (i) thermally-induced changes in DNA conformation lead to many orders of magnitude differences in instantaneous conductivity; (ii) coherent transport occurs over much longer distances than commonly assumed, leading to weak dependence of conductivity on length; (iii) while solvation in water and the positions of counterions can alter the conductivity by an order of magnitude, conformational changes are clearly the dominant effect. Furthermore, although mismatched base pairs can lower the conductivity significantly for specific DNA conformations, thermally-induced conformational fluctuations wash out this effect. Assuming exponential scaling of the current with the length, $I(L) = I_0 \exp^{-\beta L}$, β is found to be 0.18 \AA^{-1} for B-DNA. It is thus a promising nanowire candidate for nanoelectronic applications, since other molecular wires have β values between 1 and 0.2. In particular, immobilizing a partially dried poly(G)-poly(C) B-DNA on a substrate would lead to consistent conductive properties and thus be preferable for applications.

Internal Geometry, Stability and Design of Quantum Hall States

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Principal Investigator: Ravindra Bhatt
Sr. Investigator(s): F. Duncan Haldane; Princeton University
Edward Rezayi; California State University-Los Angeles
Kun Yang; Florida State University
Students: 2 Postdoctoral Fellow(s), 6 Graduate(s), 0 Undergraduate(s)
Funding: \$475,000 (2014)

PROGRAM SCOPE

We seek to build upon our recent discovery of a previously unrecognized shear deformation degree of freedom possessed by incompressible fractional quantum Hall (FQH) states, and understand its implications under various circumstances. These include multi-component anisotropic systems, inhomogeneous systems and systems in confined geometries with boundaries (e.g. quantum dots), as well as Fermi liquid states of composite fermions. We plan to extend our investigations to other anisotropic systems, and to seek systems with new, interesting phase diagrams in the FQH regime, with an eye to optimizing the stability of various phases. These include materials with various band dispersions, with different experimental geometries and sub-band structure, and systems with complex edge structures. We also propose to extend our study to cold atom based systems, which offer the possibility of tuning interactions over a wide range, and thus the hope to study new FQH phases, tuning through different phases, and new methods for probing various phases. In parallel, we will perform controlled, systematic numerical studies with the aim of achieving a fuller, quantitative understanding of

the nature and stability of the more fragile FQH states, which are candidates for topological quantum computation. Such FQH phases require reliable studies on larger sizes than is possible with exact diagonalization. We have used both the Density Matrix Renormalization Group method as well as Matrix Product State schemes in various geometries, to identify optimal geometries for various problems, and extend the size of systems that can be studied for reliable extrapolation to the thermodynamic limit. We further plan to use a real-space entanglement method to study the topology and entanglement spectrum of various FQH states.

FY 2014 HIGHLIGHTS

The past fiscal year saw the completion of several projects. In two related works, we probed the nature of quasiparticle excitations – the first exposed the internal structure of a $\nu = 1/3$ quasielectron as a composite of a charge $2e/3$ quasiparticle and a $-e/3$ quasihole; the second showed that there is a large spatial difference between quasiholes at $\nu = 1/3$ and $\nu = 7/3$. Haldane's geometrical description was generalized for anisotropic (gapless) composite fermion liquid states, which yields excellent agreement with tilted field measurements at $\nu = 1/2$ by Shayegan's group. In parallel, a comprehensive numerical study in tilted magnetic fields (and its relation to effects of band mass anisotropy) was completed, allowing direct contact with experiments of Eisenstein and Shayegan. A systematic study of FQH states in the (special) zeroth Landau level in Graphene was carried out, whose predictions are being borne out in recent experiments. Our study of reconstruction at the edge of quantum Hall phases was extended to FQH fillings $\nu = 1/3, 2/5, 2/3$ and $5/2$; in all cases but the $5/2$, edge reconstruction is driven by softening of edge spin waves in the absence of Zeeman splitting, and is prevented by Zeeman splitting. For $\nu = 5/2$, however, the edge instability is triggered by softening of the charge mode, and spin plays no role. A new study of quantum entanglement spectra of the composite Fermi liquid at $\nu = 1/2$ was carried out, using toroidal geometry and Monte-Carlo sampling. Scaling with size was found to be similar to the free Fermi case, but with twice the coefficient, suggesting a more complicated scenario. The concept of quantum entanglement was also used to study a different many-body system, namely the phenomenon of many-body localization (MBL) in the presence of large disorder. Several new results were found in this developing field, e.g. area law for entanglement entropy, and signatures of MBL in the presence of coupling to a bath present in experimental situations.

Near-Field Electrodynamics of Carbon Nanostructures

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PROGRAM SCOPE

The objective of this research is to advance the frontiers of fundamental knowledge on near-field electrodynamic processes in complex carbon nanostructures. The project seeks to explore how one can use near-fields of low-energy collective interband plasmon excitations of individual constituent carbon nanotubes to tailor optoelectronic properties of (i) double wall carbon nanotube systems and (ii) hybrid quantum systems of molecular-array/metal-atomic-wire encapsulating carbon nanotubes. Clear understanding of the properties of collective electron excitations, and how individual constituents of

complex systems communicate with one another in the near-field, and what it does to the properties of the entire complex hybrid system, is a natural prerequisite for advances ranging from new applications, such as coherent light emission, enhanced electromagnetic absorption, scattering and conversion of ambient electromagnetic radiation, to the development of new concepts for future generation carbon based plasmonic nanomaterials engineering. This research will open up new directions for fundamental nanoplasmonics and near-field optics research, currently focused mostly on metallic nanoparticles, to include a new area of nanotube plasmonics.

FY 2014 HIGHLIGHTS

(1) Exciton Bose-Einstein Condensation (BEC) in Carbon Nanotubes: We demonstrate the possibility for the exciton BEC in individual small-diameter (~1–2 nm) semiconducting carbon nanotubes. The effect occurs under the exciton-interband-plasmon coupling controlled by an external electrostatic field applied perpendicular to the nanotube axis. The effect offers a testing ground for fundamentals of condensed matter physics in one dimension and opens up perspectives to develop a tunable coherent polarized light source with carbon nanotubes. [Physical Review B 89, 045414 (2014)] (2) Bipartite Entanglement in Hybrid Carbon Nanotube Systems: We study theoretically a pair of spatially separated extrinsic atomic type species (extrinsic atoms, ions, molecules, or semiconductor quantum dots) near a metallic carbon nanotube, that are coupled both directly via the inter-atomic dipole-dipole interactions and indirectly by means of the virtual exchange by resonance plasmon excitations on the nanotube surface. We analyze how the optical preparation of the system by using strong laser pulses affects the formation and evolution of the bipartite atomic entanglement. We find generic scenarios for the entanglement evolution and formulate practical recommendations on how to optimize and control the robust bipartite atomic entanglement in hybrid carbon nanotube systems. [Chemical Physics 413, 123 (2013); J. Chem. Phys. 140, 064301 (2014)] (3) Plasmon Enhanced Raman Scattering Near a Carbon Nanotube: Quantum electrodynamics theory of the resonance Raman scattering is developed for an atom in a close proximity to a carbon nanotube. The theory predicts a dramatic enhancement of the Raman intensity in the strong atomic coupling regime to nanotube plasmon near-fields. The effect can be used in designing efficient nanotube based optical sensing substrates for single atom detection, precision spontaneous emission control, and manipulation. [Optics Express, submitted (arXiv1407.5142)]

Correlated Electrons in Reduced Dimensions

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PROGRAM SCOPE

The combination of strong correlations and reduced dimensionality can lead to the formation of exotic states of matter for which conventional “textbook” methods of condensed matter physics breakdown. An example of such states are those with so-called topological order, a type of quantum order not characterized by any local order parameter but rather by global properties, (e.g., ground state degeneracies on topologically nontrivial surfaces, fractionalized quasiparticle excitations with exotic quantum statistics, etc.). One goal of this project is to better understand topological order, and, in

particular, the intimate connection it has with the theory of fault-tolerant quantum computation. This widely appreciated connection has motivated much of the recent work which attempts to physically realize topologically ordered states with non-Abelian anyon excitations, as well as ideas for how one could essentially simulate topological order on a “conventional” quantum computer and thus have the computer inherit the built in protection of these states from decoherence, (the so-called “surface code” approach --- currently the leading candidate for realizing fault-tolerant quantum computation). The project is also focused on understanding the properties of metals with sharp Fermi surfaces but without well-defined Landau quasiparticles (and thus, again, a class of states which lies outside of standard condensed matter physics). The question of how the breakdown of Fermi liquid theory affects the quantum phase transitions which can occur in these systems, e.g., BCS (Bardeen-Cooper-Schrieffer) pairing, excitonic condensation, is actively being studied, with work focusing on the composite fermion “metal” description of the compressible $\nu=1/2$ quantum Hall state, for which the Halperin-Lee-Read theory provides a powerful theoretical framework for studying at least one flavor of non-Fermi liquid behavior.

FY 2014 HIGHLIGHTS

A two-dimensional electron gas (2DEG) in a magnetic field with Landau level filling fraction $\nu=1/2$ can enter a compressible state in which composite fermions (CFs) --- emergent excitations consisting of electrons bound to two flux quanta --- form a “metal” with a sharp Fermi surface. In bilayer systems made up of two parallel 2DEGs we studied the transition from two decoupled $\nu=1/2$ CF metals (large layer spacing) to a recently proposed interlayer coherent CF state (intermediate layer spacing). In this latter state, interlayer Coulomb repulsion leads to excitonic condensation of CFs which are then free to tunnel coherently between layers. We found this tunneling is suppressed by the layer-dependent Aharonov-Bohm phases CFs experience as they propagate through the fluctuating gauge fields in the system. This suppression leads to (1) an increase in the critical interlayer repulsion needed to drive the transition and (2) a discontinuous jump in the energy gaps to out-of-phase excitations (those involving currents with opposite signs in the two layers) at the transition. Reason (1) may account for the fact that the interlayer coherent state has not yet been observed experimentally; and reason (2) suggests that if such a transition were to be observed, the detection of a discontinuous jump in the out-of-phase energy gaps would provide indirect experimental evidence for the presence of gauge fluctuations in the system. [Phys. Rev. B 89, 085109 (2014); Editors’ Suggestion]. Voltage pulses which rapidly switch on and off the exchange interaction between two electrons have proven a useful resource for manipulating spin states in multi-quantum dot systems. We have recently obtained a new class of pulse sequences which can be used to entangle two two-level systems encoded using six electron spins. Our sequences are obtained analytically, and shed significant light on the structure of the numerically obtained sequences found previously. [Phys. Rev. B 89, 085109 (2014)].

Strongly Correlated Electrons: Ground States, Excited States, and Transport

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Funding: \$630,000 (2014-2016)

PROGRAM SCOPE

The aim of the present project is simple. Prof Roberto Car will develop and test a new ground-state method, denoted OP-NOFT (Occupation Probabilities - Natural Orbital Functional Theory), on molecules and solids. Simultaneously, Burke's group will develop a one-dimensional version, and benchmark it against DMRG (Density Matrix Renormalization Group) calculations, which provide essentially exact solutions. Burke's group will use their scattering methodology to extract conductances from sequences of excited-state energies of exact finite-size molecular calculations in 1D using DMRG. These exact conductances will be compared to Kohn-Sham conductances, found by inverting the KS equations for the OP-NOFT ground-state density. Once it is found where these agree (which should be the typical case for zero-temperature, weak-bias systems dominated by a single channel), both groups will collaborate on performing full chemically realistic calculations in 3D. OP-NOFT has the potential to become a standard method in quantum chemistry. It can break bonds correctly, with a much lower computational cost than traditional alternatives and much higher accuracy than standard DFT treatments. Its ability to accurately include strong static correlation makes it ideal for dealing with the inaccuracies of DFT transport calculations for organic molecules.

FY 2014 HIGHLIGHTS

The Burke group has two major projects is being written up for this period. The first is a large study of the relation between density functional theory and lattice models, using the asymmetric Hubbard dimer as an explicit example. This 35-page paper will be submitted to reviews of modern physics, and will serve as a starting point for all future work involving strong correlation. In this case, OP-NOFT yields an exact solution. This work involves the graduate student, plus an international collaboration with a many-body theorist in Oviedo, Spain, Jaime Ferrer Rodriguez. The second is an important demonstration that Coulomb blockade physics can be extracted from a non-local ground-state density functional calculation, without invoking time-dependent density functional theory. This provides a very different view of how DFT describes the underlying physics, counter to many suggestions in the literature. This work is in collaboration with Zhenfei Liu at Lawrence Berkeley National Lab. Two projects were conducted by Car: (1) The OP-NOFT theory was generalized beyond zero seniority (doubly occupied natural orbitals only). A paper is under review at the Proceedings of the National Academy of Science, in collaboration with Morrel H. Cohen (Princeton and Rutgers) and Ralph Gebauer (ICTP, Trieste (Italy)). Rob A. DiStasio, a postdoc at Princeton, is applying this to the homogeneous electron gas. (2) The concept of fragile Mott insulators (FMI) was extended to ring-shaped molecules with repulsive Hubbard interaction threaded by a half-quantum of magnetic flux. The FMI is an insulating ground state that cannot be adiabatically connected to a single Slater determinant. Electron correlations produce a rich phase diagram in these simple molecular systems. Lukas Muechler, a graduate student at Princeton is the author of a Physical Review B paper, in collaboration with Joseph Maciejko (University of Alberta, Edmonton) and Titus Neupert (Princeton Center for Theoretical Science).

Physics of Graphene

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PROGRAM SCOPE

The research in this program involves theoretical investigations of electronic, optical and mechanical properties of graphene and its derivatives, such as bi-layer graphene, graphene heterostructures, strained graphene, as well as graphene on various surfaces. One line of research has been development of theoretical models that support graphene's large array of possible technological applications. For example one of our goals has been the understanding of surface plasmons and spin relaxation mechanisms in graphene, related to novel optoelectronics and spintronics applications. Our current research focus is on understanding the role of correlations in graphene under mechanical deformations, such as strain. The main goal is to describe the mutual interplay between strain and electron-electron interactions which could lead to the formation of novel electronic phases with strongly modified electronic, magnetic and optical properties. This direction of research contributes to deeper understanding of interactions in graphene - a subject at the forefront of research on graphene and its derivatives.

FY 2014 HIGHLIGHTS

The main accomplishments in the past year have been in the following areas: 1.) We have discovered that uniaxial strain deformations can have a major effect on van der Waals interactions between graphene sheets. In particular strong, order of magnitude enhancement of the vdW interaction is possible under strain. The van der Waals interaction is also very sensitive to the electron-electron interaction strength, and the renormalization of the Coulomb interactions can in fact lead to modification of the conventional distance dependence of the dispersion forces - an effect unique to graphene. These results can open up a whole new direction in the field of van der Waals heterostructures. 2.) We have investigated the phase diagram of the Anderson impurity model describing localized magnetic states, due to electron correlation, on adatoms in strained graphene. Detailed predictions were made for the values of the Hubbard U and strain necessary to generate magnetic moments. We have studied the influence of uniaxial strain on the ferromagnetic exchange instability in graphene and have found that itinerant magnetism can occur at much smaller (strain-dependent) value of the electron-electron interactions, relative to the unstrained isotropic graphene. This can lead to magnetism, with rather large magnetization, in strongly anisotropic graphene-based systems. 3.) We have studied graphene on Hexagonal Boron Nitride where, due to incommensuration effects with the substrate, graphene can develop gapped low energy modes that spatially conform into a triangular superlattice of quantum rings. In the presence of these modes, we have shown that Coulomb interactions can lead to spontaneous formation of chiral loop currents in bulk and to macroscopic spin-valley order at zero temperature. Thus we have made the first prediction for an exotic many-body state in graphene on Boron Nitride which can possibly lead to unconventional experimental realization of valley order.

Quantum Nanowire Multi-Connections

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Funding:	\$140,000 (2014)

PROGRAM SCOPE

The characterization of interacting topological phases of matter is one of the major goals of the BES supported work. The recently discovered prospect of realizing fractional quantum Hall (FQH) states with the inclusion of short-range interactions in lattice models featuring fractionally filled, topologically non-trivial bands has garnered considerable interest. Apart from a paradigmatic extension of the FQH effect to lattices, these states, called fractional Chern insulators (FCI), arise without an externally applied magnetic field. Because the energy scales are those dictated by interactions and hoppings over lattice distances, the FCIs are an important conceptual step towards realizations of fractionalized states at high temperatures. In addition to the investigation of interacting topological states of matter, the BES supported work is also directed at advancing our fundamental understanding of periodically driven, non-equilibrium quantum systems. Non-equilibrium quantum systems stand at a natural frontier of physics that is only beginning to be probed by theory and experiment. Particularly exciting is the possibility of attaining material properties that are unreachable at equilibrium. We are investigating fundamental aspects of non-equilibrium condensed matter theory, most notably we want to understand the nature of the steady states in systems that are driven by an AC electric field while in contact with a thermal reservoir. The presence of dissipation due to the bath is characteristic of solid state systems, and is to be contrasted with the case of artificial structures built on optical lattices, where the systems are well isolated from their environment.

FY 2014 HIGHLIGHTS

We studied analytically a systematic way to construct two-dimensional topological states starting from one-dimensional quantum wires that are coupled together by electron tunneling. In this construction, non-chiral Luttinger liquids are placed in a periodic array of coupled wires. We also analyzed manifestations of topological order in time-reversal-symmetric fractional topological liquids where the edge modes on boundaries are fully gapped by appropriate backscattering terms. In the absence of gapless edge modes, we showed that there is a ground state degeneracy for systems defined on planar surfaces with holes. We also investigated the possibility of measuring the topological ground state degeneracy with calorimetry. Many of the highlights of the BES supported work on interacting topological phases of matter were presented in an article prepared for the proceedings of the Nobel symposium on “New forms of matter: topological insulators and superconductors” that took place in June 2014 in Stockholm, Sweden. The PI presented an invited talk at this symposium with the results of this DOE supported research. Within the scope of the research on non-equilibrium quantum systems, we unveiled a new route to superconductivity that relies on establishing a non-equilibrium population of carriers via optical pumping. Specifically, we showed that optically pumped semiconductors can exhibit superconductivity. We computed the finite superconducting gap and argued that the mechanism can be induced through both attractive and repulsive interactions and is robust to high temperatures.

Quantum Embedding for Correlated Electronic Structure in Large Systems and the Condensed Phase

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Funding:	\$155,000 (2014)

PROGRAM SCOPE

The main objective of the work is to explore, extend, and establish a new technique for bulk materials simulation: density matrix embedding theory (DMET). DMET is a theoretical framework to map bulk problems of correlated electrons, phonons, spin, and spectra into finite correlated problems, which may then be solved accurately using standard techniques. The research has the twin goals of expanding the DMET formalism to new situations (e.g. spin systems, topologically ordered states, long-range interactions, finite temperature, and real-time dynamics) as well as applying DMET to solve long-standing correlated electron materials problems involving quantum magnetism and high temperature superconductivity.

FY 2014 HIGHLIGHTS

This year, we have extended DMET in several directions. These include: calculation of spectral/dynamical quantities; mixed fermion-boson systems (to treat electron-phonon coupling); and incorporating DMET into quantum-classical treatments (i.e. QM/MM). We have further been pushing DMET to more and more challenging applications. We applied DMET to resolve the issue of the intermediate phase of the Hubbard honeycomb model, the source of much controversy. DMET with large clusters definitively show that (i) there is no spin-liquid phase (ii) at intermediate couplings the system is close to a special hexagonal cluster order. More ambitiously, we have also been using DMET with large clusters extrapolated to the thermodynamic limit to produce a definitive ground-state phase diagram of the 2D Hubbard model on a square lattice, with rigorous error bars. The 2D Hubbard model is the fundamental model of high T_c superconductivity, and understanding its ground-state behaviour is a long-standing challenge. Using DMET, we have been able to compute the ground-state phase diagram to very high accuracy, better than $0.006t$ across the whole phase diagram, well below the superconducting T_c . Many basic questions about the ground-state diagram (such as even the presence of superconductivity) have long been contentious. Our converged phase diagram demonstrates that there is robust superconductivity in the ground-state, as well as rich competing magnetic, charge, and pair density wave phenomena which emerges at large interaction strength. The invention of DMET was specifically mentioned in the National Academy of Sciences Award for Initiatives in Research; and many groups have also started exploring this technique in this year.

Scalable Computational Tools for Discovery and Design: Excited State Phenomena in Energy Materials

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Funding: \$711,495 (2014)

PROGRAM SCOPE

The objective of this project is to develop and implement new methods and theories to elucidate and predict excited electronic state phenomena in energy related materials. Understanding excited state phenomena requires knowledge of both the ground state properties and the related many-electron interactions with excited states, which may involve structural and orbital relaxations. As such, quantitative predictions for excited state phenomena are at the leading edge of current theories for the electronic structure of materials. Advanced algorithms and many-body perturbation theory will be used to predict quasiparticle excitations and lifetimes, optical spectra, excited-state energy surfaces, transport properties, and other excited-state properties/processes. Excited-state properties will be addressed in an interacting Green's functions formalism within many-body perturbation theory. Quasiparticle spectra will be computed within the GW approximation for the electron self-energy, and two-particle optical excitations will be calculated within a Bethe-Salpeter equation approach, including electron-hole interactions. Ground-state properties will be addressed with pseudopotentials within density functional theory. A solution of the Kohn-Sham problem for large scale systems will be implemented within real space using newly developed "parallel" eigensolvers. Science applications will focus on molecular organic assemblies and transition-metal oxides, which are examples of two important classes of materials that promise low-cost, sustainable solar energy conversion. Although structurally distinct, these materials classes share common chemical attributes: highly-localized, sometimes strongly-correlated electronic states and, in some instances, appreciable noncovalent interactions. Additionally, interfaces (both metal-semiconductor and organic-organic) are crucial to energy conversion, and in many cases, their impact on device function is not well understood.

FY 2014 HIGHLIGHTS

Significant advances in algorithms and efficacious coding were achieved for both ground state and excited state codes. With respect to the ground state code, new eigensolvers were implemented to compute eigenvalues within an energy window. This approach adds an additional level of parallelism and allows one to address a key bottleneck: The diagonalization of a large, dense matrix. A new procedure for expediting matrix-vector multiplications was developed that will have wide spread applications. Continued work on interfacing excited state and ground state codes were executed. Materials applications were also carried out. Data mining techniques for predicting the properties of materials were developed. New methods for computing coulombic interactions of charged defects in nanoscale materials were implemented. Studies in fundamental defects, i.e. the oxygen vacancy in strontium titanate compounds were carried out, and surface/interfacial properties of these compounds with respect to highly correlated phenomena were explored.

Theory of Functionalized Nanostructures

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PROGRAM SCOPE

The theme of this research program is to develop and implement theoretical methods for predicting and understanding the properties of functionalized matter at the nanoscale. The nanostructures of interest are those composed of electronic materials, e.g., semiconductors like Si or ZnO. Within the nano regime, phenomena occur that are characteristic of neither the atomic limit nor the macroscopic limit. Such phenomena can have direct consequences for characterizing properties of materials. To capitalize properly on predicting such phenomena in this transition (nano) regime, a deeper understanding of the electronic, optical, and magnetic properties of matter will be required. Areas of research encompassed by this work include (1) the electronic and structural properties of dopants relevant for the functionalization of nanostructures (nanocrystals, nanowires, and nanofilms), including both magnetic and non-magnetic dopants; and (2) the evolution of bulk-like electronic, magnetic, and structural properties from the nano to macro scale. The proposed areas of research will enhance our understanding of nanomaterials and the role of quantum confinement and dimensionality at the nanoscale.

FY 2014 HIGHLIGHTS

Research within this program focused on two applications during this time period. One application involved the development of a new model for predicting the properties of charged defects in nanostructures. In particular, an “effective capacitance” model was developed for computing the electronic properties of charged defects in crystals and nanostructures. This model avoids many of the complexities occurring when supercell geometries are employed. Such geometries result in long range coulomb forces involving divergent terms, which often require artificial compensating background charge densities to achieve converged energies. The capacitance model avoids compensating backgrounds. It was employed to determine when heavily doped nanowires become metallic. The other application involved examining the role of dopants on vibrational modes in the Raman spectra of P-doped Si nanocrystals. Raman spectra is a convenient probe to determine the bonding characteristics of materials, e.g., the existence of particular chemical bonds. The P-Si bond does not significantly change the vibrational modes of the nanocrystal, but does break symmetry and strongly alters the Raman spectra. As a consequence, Raman measurements can be used to assess the bond site geometry of doped nanocrystals.

A Computational Approach to Complex Junctions and Interfaces

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Funding:	\$180,000 (2014)

PROGRAM SCOPE

The focus of our DOE BES funded program is to understand physical processes at interfaces and across nanojunctions via state-of-the-art, large-scale computation and simulation. Theoretical treatment for electronic degrees of freedom in our investigations is mainly at the level of density functional theory with generalized gradient approximations. Various theories, methods and techniques including

scattering theory, non-equilibrium green functions, the density matrix method, Boltzmann transport theory, classical molecular dynamics, and van der Waals corrections etc. will be used to calculate physical and chemical quantities needed for addressing problems and issues. We study problems in a number of complex interfaces and junctions including a) electron transport through metal-azobenzene-molecule-metal junctions, where the molecule can transform between trans and cis configurations in response to light excitation; b) bonding, atom diffusion, and magnetization in systems containing the tris(8-hydroxy-quinolino)aluminum (Alq3) molecule on magnetic surfaces and between two magnetic leads, for its role as insulator spacer in magnetic tunneling junctions; c) electron dynamics coupled with structural relaxation and phonon-electron interaction after photo-excitation in carbon nanotubes and graphene that are functionalized by adsorbed organic molecule, because understanding such processes may provide hints of mechanisms for photon-electron current conversion; and finally d) interfacial electronic and magnetic properties. One common theme unifying these systems is that interfacial structure has critical effects on properties, and our investigations based on first-principles can provide guidance, not only interpretation, for experiments. Our effort also includes major development of theoretical methods for studying electron transport.

FY 2014 HIGHLIGHTS

We have shown that the conformational dependence of the Coulomb charging energy of a nanocluster leads to a giant electroresistance, where charging induced conformational distortion changes the blockade voltage. The intricate interplay between charging and conformation change is demonstrated in a nanocluster Zn_3O_4 by combining a first-principles calculation with a temperature-dependent transport model. The predicted hysteretic Coulomb blockade staircase in the current-voltage curve adds another dimension to the rich phenomena of tunneling electroresistance. The new mechanism provides a better controlled and repeatable platform to study conformational electroresistance. We have completed the development of a hybrid approach for electron transport. We applied the method to study conductance cross Ag-silicence-Ag junctions and Ni-hBN-Ni junctions, two systems that can be realized in laboratory. When the number of layers of an insulator 2D crystal is small, the calculated transmission coefficient per channel is a fraction of 1, the Landauer equation is no longer adequate. Our hybrid scheme that combines NEGF (Non-Equilibrium Green's Function) techniques, scattering theory, and semi-classical Boltzmann transport theory to compute the conductance of well conducting junctions. We have found a quantitative limit for transmission coefficient below which the Landauer method and the Boltzmann equation agree. We have also implemented the GW method in a newly developed all-electron band structure code, EXCITING+ (also called modified ELK). We used the new GW code to study a group of semiconductors.

Disorder, Dynamics, and Transport in Quantum Magnets

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PROGRAM SCOPE

Within the current project we perform a set of interrelated theoretical studies with the goal of deepening our understanding of the dynamical and transport phenomena in quantum magnets, in particular the phenomena induced or influenced by disorder. Fundamentally, spin dynamics and magneto-thermal transport are widely open fields of study with the problems of mutual interactions of spin and phonon excitations, role of the dimensionality of spin system, and effects of disorder being largely unexplored. The experimental discoveries of a variety of unusually strong field-dependent phenomena and of the signatures of quasi-ballistic transport in a number of materials contribute to the excitement in this area and call for theoretical explanation. We expect our studies to advance basic knowledge of the physical properties of a diverse group of materials and yield predictions of new phenomena in them.

FY 2014 HIGHLIGHTS

We have recently made a significant progress in theoretical understanding of the quantum effects in kagome-lattice antiferromagnets and provided deep insight into the quantum order-by-disorder mechanism, which is important for the broad class of frustrated systems. We have also challenged general expectation that quantum fluctuations simply follow thermal ones in selecting the ground state and presented a rare example of the situation when quantum order-by-disorder defies this trend and yields the ground state that is different from one favored by thermal fluctuations. We have demonstrated that the order selection is generated by topologically non-trivial tunneling processes, making loops around elementary hexagons. We have proposed a tentative phase diagram of the model and suggested further theoretical studies. This recent progress also paves the way for the future studies of the unusual spin dynamics and calculations of the dynamical structure factor of the realistic kagome-lattice antiferromagnets such as iron-jarosite.

First Principles Investigation of Complex Materials Properties

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PROGRAM SCOPE

This project concentrates on studying complex materials properties using first-principles electronic-structure methods. The computational tools that we will employ include density functional theory (DFT) within the local-density or generalized gradient approximation (LDA or GGA), the pseudopotential method with a plane-wave basis, quantum Monte Carlo (QMC) methods for systems with considerable electron correlation, density-functional perturbation theory (DFPT) for the vibrational properties, and nonequilibrium Green's function methods for electron transport. Our goal is to unambiguously explain the phenomena observed in the experiment and to reliably predict new materials properties. Recently, we have focused on low-dimensional electronic systems that exhibit interesting physics not present in typical bulk systems. In particular, we have concentrated on studying the interesting properties of graphene, metal thin films, and semiconductor nanowires.

FY 2014 HIGHLIGHTS

We have performed first-principles calculations to illustrate that it is possible to synthesize silicene and germanene on the graphene substrate without destroying graphene's characteristic Dirac-fermion-like linear dispersion around its Dirac points, due to the weak van der Waals interlayer interaction. In addition, multiple phases of single crystalline silicene or germanene with different orientations could coexist at room temperature based on our energetics analysis. The substrate breaks the sublattice symmetry in silicene and germanene and induces a gap at the Dirac point. For silicene on graphene, the gap could be as large as 57 meV. For germanene on graphene, the gap created by the substrate effect is of the same order as that induced by the spin-orbit coupling (SOC) effect. The interplay between the substrate and SOC effects could be used for further band-gap manipulations. Our fundamental study of the electronic structure and energetics of these silicene/graphene and germanene/graphene bilayers may provide important insight for other two-dimensional van der Waals heterostructures.

Interplay Between Superconductivity and Magnetism in Iron-Based Superconductors

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

The goal of the project is to understand theoretically the interplay between superconductivity, magnetism, and nematic order in Iron-based superconductors (FeSCs), which currently attract high attention in the physics community. The primary goals are to understand the mechanism of superconductivity, the origin of magnetism and of the nematic order which accompanies structural distortion, the co-existence regimes of different orders, and the observed pseudogap-like behavior in the normal state. My research explores the idea that superconductivity in FeSCs is of electronic origin and is caused by the exchange of spin-fluctuations, enhanced due to close proximity to antiferromagnetism. The spin-fluctuation approach has been discussed over a number of years for the cuprates, where it gives rise to a d-wave superconductivity. For the pnictides, which are multi-band materials, the spin-fluctuation approach leads to an attraction in both d-wave and extended s-wave (s^+) channels, and it becomes an issue what type of order the system chooses at a given doping. Besides, due to the presence of multiple Fermi surface sheets, both s-wave and d-wave gaps can have quite non-trivial forms, e.g., an s^+ gap may have nodes. The understanding of magnetically-mediated superconductivity in FeSCs will contribute to a generic understanding of the pairing of fermions near quantum-critical points -- the problems ranging from s-wave pairing by soft optical phonons to color superconductivity of quarks mediated by a gluon exchange. Antiferromagnetism and superconductivity are neighbors in many systems: cuprates, heavy-fermion materials, 5d- oxides, cobaltates, and the study of the interplay between magnetic and superconductivity should have impact on these systems as well.

FY 2014 HIGHLIGHTS

My research in 2013-2014 was focused on properties of Fe-based superconductors, charge order in the cuprates, collective modes in near-critical Fermi liquids, properties of anisotropic triangular antiferromagnets and superconductivity of fermions on hexagonal lattices. All these works were supported only by DOE. The analysis of Fe-based superconductivity has been the primary subject of my DOE project and below I summarize my main results on Fe-based materials. (i) I analyzed how magnetic and nematic transition lines behave under the superconducting dome. (ii) I wrote two review papers on the issue of superconductivity from nominally repulsive electron-electron interaction, (iii) I studied spin resonance in the superconducting state of recently discovered alkali-intercalated iron selenide materials $A_x\text{Fe}_{2-y}\text{Se}_2$ ($A = \text{K, Rb, Cs}$). I considered the novel s^+ superconducting state recently proposed by us, with superconducting gap changing sign between the hybridized electron pockets. We argued that such a state supports a spin resonance. I computed the dynamical structure factor and showed that it is consistent with the results of inelastic neutron scattering. (iv) I studied Raman scattering in the superconducting state of $A_x\text{Fe}_{2-y}\text{Se}_2$. I developed the theory of Raman scattering assuming that the ground state has s -wave symmetry but d -wave is a close second. (v) I wrote a review on different microscopic models for nematicity in the iron pnictides, and on how nematicity is linked to other ordered states of the global phase diagram of these materials – magnetism and superconductivity. (vi) I analyzed the structure of the pairing interaction and superconducting gap in LiFeAs by decomposing the pairing interaction for various k_z wavevector cuts in the Brillouin zone into s - and d -wave components and by studying the leading superconducting instabilities. (vii) I analyzed superconductivity in the coexistence region with spin-density-wave order in weakly doped Fe-pnictides.

Dynamics of the Magnetic Flux in Superconductors

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Funding: \$240,000 (2014-2016)

PROGRAM SCOPE

The work on the DOE grant at Lehman College is advancing the knowledge of physics of superconductors and their potential applications by addressing fundamental and practical questions of the physics of superconducting materials and circuits. Recently pursued research topics include macroscopic quantum tunneling of the magnetic flux in type-I superconductors, dynamics of topological defects in parental compounds of high-temperature superconductors, effects of topological defects generated by random fields on the long-range order in flux lattices and spin systems, manipulation of nanomagnets by Josephson junctions, and decoherence of flux qubits. The ongoing work and research planned for the nearest future include analytical and large scale numerical studies of the effects of random fields on correlations in superconductors and random magnets, stability of skyrmions in the presence of random fields and lattice deformations, and coupled quantum dynamics of nanomagnets and Josephson junctions. This work will provide deeper insight into glassy properties of flux lattices that are responsible for the critical currents, may help understand the interplay between non-linear spin fluctuations and lattice deformations in high-temperature superconductors, and will suggest applications of Josephson devices for precise measurements of quantum nanomagnetic phenomena.

FY 2014 HIGHLIGHTS

We have studied the connection between topology and long-range behavior of random-field systems. This problem is related to critical currents in type-II superconductors and to the coercivity of disordered magnets. Years of studies of thermodynamic equilibrium of random-field systems by many authors rendered inconclusive results. Meanwhile real systems with disorder rarely reach thermodynamic equilibrium. Our focus has been on reversible versus irreversible behavior. Through rigorous mathematical arguments, supported by numerical simulations on lattices containing up to one billion sites, we have demonstrated that the behavior of the random-field system is governed by topology that depends on the relation between the number of components of the order parameter and dimensionality of space. Presence of topological defects results in irreversible glassy behavior, while in the absence of such defects the system exhibits reversible behavior with correlations decaying exponentially at large distances. In a separate work we have studied Josephson tunneling through a circularly polarized magnetic disc with a vortex, forming a weak link between two superconductors. Our focus has been on the possibility of the detection of the tiny movements of the vortex, due to thermal jumps or quantum tunneling, via measurement of the tunneling current. [1] D. A. Garanin, E. M. Chudnovsky, and T. Proctor, Europhysics Letters 103, 67009 (2013). [2] D. A. Garanin, E. M. Chudnovsky, and T. Proctor, Physical Review B 88, 224418 (2013). [3] T. Proctor, D. A. Garanin, and E. M. Chudnovsky, Physical Review Letters 112, 097201 (2014). [4] D. A. Garanin and E. M. Chudnovsky, Cond-mat arXiv: 1406.1165. 5. R. Zarzuela, E. M. Chudnovsky, and J. Tejada, Cond-mat arXiv: 1407.5419.

Theory of Layered Organic and Inorganic Materials with Charge-Spin Frustration

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Funding: \$150,000 (2014)

PROGRAM SCOPE

In a frustrated material the lattice arrangement prevents local energy constraints from being satisfied, leading to a large degeneracy of quantum states and highly unusual electronic properties. Most theoretical work to understand frustration has been carried out on quantum spin models, where charge degrees of freedom have been frozen out. In this project we investigate materials with lattice frustration where instead charge as well as spin degrees of freedom remain important at low temperatures. This theoretical work will be applied to a number of quasi-two dimensional materials, including the organic charge-transfer salt superconductors and layered cobaltates. We will focus in particular on whether frustration is a key element of the unconventional superconductivity found in many of these materials.

FY 2014 HIGHLIGHTS

We developed a correlated-electron minimal model for the normal state of metal-intercalated phenanthrenes. Exact finite cluster calculations showed that while the systems with molecular charges of -1 and -2 are one- and two-band Mott-Hubbard semiconductors, respectively, molecular charge -3 gives two nearly 3/4-filled bands. This carrier density per molecular orbital is nearly the same in the

normal state of the superconducting aromatics and organic charge-transfer solids, and may be the key to understanding unconventional superconductivity in the family of doped polycyclic aromatic hydrocarbons. Importantly, we believe that our work gives a hint to the correct mechanism of superconductivity in the metal-doped fullerides, which remains to be understood two decades after their discovery. We performed the first large-scale correlated-electron calculation of the conducting layer of the organic superconductor family κ -(BEDT-TTF)_{2X}, without assuming an effective 1/2-filled band description. Our results show that within the single-band Hubbard model the system remains a correlated metal even for very strong onsite Coulomb interaction U , with no signs of charge or spin ordering. This may explain why long-range antiferromagnetic order is only found experimentally in few members of the family. We revisited the theory of the spin-Peierls (SP) state in the organic salt (TMTTF)_{2X}. We showed that claims that two distinct SP exist here were a result of poor parameter choices in the two-dimensional model. This work led to a further study of the bond distortion pattern in 1/4-filled SP materials and updated phase diagram for the one-dimensional extended Hubbard model.

Spin and Orbital Physics in Novel Correlated Materials

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Funding: \$150,000 (2014)

PROGRAM SCOPE

This theoretical project seeks to further our understanding of materials in which the strong magnetic interactions between the electrons give rise to new classes of emergent behavior. There are three areas of focus: (1) Topological Kondo insulators. Kondo insulators are a class of magnetic material where electron screening of local moments drives a crossover from a metal to an insulator at low temperatures. Our proposal in 2010 that certain Kondo insulators are topological, with protected metallic surfaces, has attracted a lot of interest, especially with the confirmation that the Kondo insulator Samarium Hexaboride is topological. This material is of particular interest, because it has a much higher bulk resistivity than other topological insulators, moreover, the strong interactions can induce novel phase transitions at the surface. Our research aims to understand the properties and instabilities of the surface states, and the bulk. (2) Iron Based Superconductors. We are studying the multi-orbital character of the paired state in these materials: current theories assume that the superconducting pairing is orbitally diagonal; we have discovered a much larger class of orbitally entangled states, some with the s-plus-minus symmetry thought to exist in many of these materials. We are trying to link changes in the orbital entanglement with the observed sudden phase transitions from fully gapped to nodal superconductivity. (3) Two dimensional Frustrated Magnetism. Here we seek to understand how frustration in two dimensions can overcome the Hohenberg Mermin Wagner theorem, and drive emergent finite temperature order in a Heisenberg antiferromagnet. We are studying the frustrated honeycomb-triangular lattice, where we believe there may be a finite temperature power-law phase despite the Heisenberg symmetry.

FY 2014 HIGHLIGHTS

(1) Topological Kondo Insulators (TKI's). One of the unsolved paradoxes of SmB_6 , is that the conducting surface states are 'light', with a Fermi velocity that is many times smaller than predicted by the current 'heavy electron' theories. We have discovered that the surfaces of topological Kondo insulators are prone to 'Kondo breakdown', where the screening clouds around the surface magnetic moments break-down. This effect releases charge into the surface states, driving them much lighter, providing a natural explanation of experiments. This work is currently in review with Physical Review Letters. (2) Iron based Superconductors: (IBSC). We have shown that the chirality of d-bands in IBSCs act as orbital Rashba fields, mixing motional and internal orbital angular momenta of the pairs. The atomic orbitals can be regarded as $S=2$ local moments coupled to the orbital $L=2$ motion of the Cooper pairs. If our theory is correct, then the condensate of the IBSCs can exist in two states - a low spin, IBSCs can exist in two states - a low spin s^+ -wave and a high-spin nodal g -wave state. With this theory we are able to account for the unusual properties of KFe_2Se_2 , which undergoes a nodal-fully gapped transition under pressure. This work is currently under review with Nature Physics. (3) Frustrated Magnetism. We have just published a long paper on our studies of a two dimensional Heisenberg antiferromagnet with an interpenetrating hexagonal and honeycomb lattice. Here, fluctuations drive the development of $p=6$ state Clock order between the two lattices. At an intermediate temperature, this Heisenberg magnet displays an emergent finite temperature Kosterlitz Thouless transition in a Heisenberg antiferromagnet. To carry out the rather involved scaling of the spin-wave stiffnesses needed for this project, we applied a method called 'Ricci Flow' borrowed from String Theory and Number Theory. This is the first work to demonstrate the practical application of Friedan scaling to a 2D antiferromagnet.

First-Principles Calculation of Vibrational Mode Lifetimes in Complex Materials

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Funding: \$130,000 (2014)

PROGRAM SCOPE

In this project we will develop, test, and apply a new, more efficient method for calculating vibrational mode lifetimes in solids. The method, originally proposed in 2010 by Ted Dickel and Murray Daw, is based on ensemble averages of appropriate functions in phase space that can be carried out by conventional Monte Carlo. The calculation requires a means of calculating interatomic forces. The ultimate goal is to implement the method using forces from an existing first-principles electronic structure code, but the first phase focused on implementation with an empirical potentials code. Recapping the project objectives: (i) Test the proposed approximation on simple models of vibrating lattices, and further understand its range of validity. (ii) Implement the method as a 'wrapper program' (Jazz) for an existing empirical potentials code (LAMMPS). (iii) Use the method to investigate vibrational mode lifetimes in several interesting materials. (iv) Implement the method as a 'wrapper program' for an existing first-principles electronic structure code, and to apply that new method to some interesting examples. This year we completed the first two objectives and began working on the last two.

FY 2014 HIGHLIGHTS

(1) The fourth-moment approximation is very successful in predicting the lifetimes of vibrational modes in most solids. We obtained this conclusion by analyzing extensive ensemble Molecular Dynamics calculations (MD runs averaged over an ensemble of initial conditions) of vibrating solids. We concluded that this approximation works well because the density of states of each individual mode is dominated by a single, broadened peak, which is typical of normal modes in solids. The second moment tracks the overall frequency of the mode, which shifts with temperature (so-called “quasi-harmonic” effect). The fourth moment provides a measure of the temperature-dependent broadening due to anharmonicity beyond that captured by the quasiharmonic shift. We also surmised that atypical systems – such as those with multiple minima (so-called “rattlers”, for example) – will likely require further development. (2) We have produced and published a code for calculating vibrational mode lifetimes based on empirical potentials. The code (“Jazz”) is implemented as a Python wrapper for LAMMPS (a multi-purpose empirical potential code originated and maintained by Sandia National Labs). The anharmonic character of the normal modes is analyzed via the Monte Carlo-based moments approximation. It is distributed as open-source software and can be downloaded from <http://jazzforlammps.sourceforge.net/>. Jazz will work for any material available in LAMMPS. (3) We have begun a study of vibrational modes in several systems of interest. In 3D solids, we are studying the lifetimes of modes in Si- and Ge-based clathrates. In nano-structures, we are studying the modes of nanowires, nanotubes, and graphene sheets. In all systems, we are investigating also the effects of native defects on the mode lifetimes. (4) We have carried out initial tests using the first-principles electronic structure code SOCORRO (originated and maintained by Sandia National Labs).

Time-Dependent Density-Functional Theory of Charge, Energy and Spin Transport and Dynamics in Nanoscale Systems

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Funding: \$630,000 (2014-2016)

PROGRAM SCOPE

The trend toward extreme miniaturization of electronic devices has fueled a lot of theoretical investigations aimed at understanding the electrical transport properties of quantum-mechanical systems. However, despite considerable progress, this problem still represents a formidable challenge since one has to deal with a quantum many-body system driven out of equilibrium. In this project, we continue our work towards a complete formulation of the transport problem using Time-Dependent Density-Functional Theories (TDDFTs), by which we understand not only the traditional time-dependent DFT, but also our recent derivatives and generalizations, such as the time-dependent current-density functional theory, the quantum continuum mechanics, the stochastic time-dependent current-DFT for open quantum systems, and the very recently developed thermal TDDFT, which includes energy density and the associated inverse temperature field as basic variables. More specifically, the project seeks further theoretical development in the following areas: (i) Calculation of dynamical many-body corrections to the electrical resistance of nanoscale conductors (e.g., many-body corrections to the Landauer formula); (ii) “Luttinger-field” description of thermoelectric phenomena; (iii) Development of

new exchange-correlation energy functionals for charge, spin, and energy dynamics; (iv) Calculations of transport coefficients (viscosity, thermal conductivity, spin conductivity) of electron liquids in the hydrodynamic regime, and understanding of transport properties of nanoscale and atomic systems; (v) *Ab initio* theory of entanglement in atoms, molecules, and nanoscale systems; (vi) Development of the quantum continuum mechanics, towards a “density-functionalized” form of hydrodynamics.

FY 2014 HIGHLIGHTS

(i) Our papers 'Density Functional Theory of Thermoelectric Phenomena', by F. G. Eich, M. Di Ventura, and G. Vignale, Phys. Rev. Lett. 112, 196401 (2014) and “Luttinger field approach to thermoelectric transport in nanoscale conductors”, by F. G. Eich, A. Principi, M. Di Ventura, and G. Vignale, Phys. Rev. B 90, 115116 (2014), present a novel approach to the study of thermoelectric phenomena, based on the introduction of a Luttinger field that couples locally to the energy density. We have shown that our approach reduces to Landauer’s theory in the linear regime, when dynamical corrections can be ignored; (ii) In 'Transverse and longitudinal gradients of the spin magnetization in Spin-Density-Functional Theory', arXiv:1309.4905, F. G. Eich, S. Pittalis, G. Vignale, Physical Review B 88, 245102 (2013) we proposed a new strategy for the construction of an exchange-correlation functional for non-collinear spin DFT; (iii) With Alessandro Principi we performed extensive studies of transport coefficients of electron liquids, and discovered a violation of the Wiedemann-Franz law, connecting the thermal and electrical conductivity of an electronic system in the hydrodynamic regime (see 'Violation of the Wiedemann-Franz law in hydrodynamic electron liquids” A. Principi and G. Vignale, arXiv:1406.2940, submitted to Phys. Rev. Lett.). We have also completed careful studies of plasmon losses in graphene, including electron-electron, electron-impurity, and electron-phonon interactions, finding detailed agreement between theory and experiment [See 'Highly confined low-loss plasmons in graphene-boron nitride heterostructures', by Woessner *et al.*, Nature Materials (2014) DOI: 10.1038/NMAT416]; (iv) Together with Sebastiano Peotta and in collaboration with C.-C. Chien we studied the transport properties of atomic gases subject to gauge fields using exact time-dependent DMRG (Density Matrix Renormalization Group) for conditions under which a quasi-steady state is formed.

EARLY CAREER: Competing Orders in Correlated Materials: Impact of Disorder and Non-Equilibrium Perturbations

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Funding: \$750,000 (2014-2018)

PROGRAM SCOPE

The goal of this project is to explore, understand, and ultimately control the competing electronic ordered states ubiquitously present in correlated materials. These unique systems not only provide empirical access to the collective behavior of interacting electrons, unveiling fundamental properties of quantum matter, but also serve as cornerstones for exciting technological applications. As different parameters of these correlated materials are tuned, distinct competing electronic ordered states emerge, such as magnetism, unconventional superconductivity, charge order, and orbital order. On the one hand, this competition suppresses the onset of desired phases, particularly of high-temperature

superconductivity. On the other hand, the enlarged ground-state degeneracy associated with these multiple many-body instabilities can give rise to unusual inhomogeneous correlated normal states, such as electronic smectic and nematic phases. To advance our understanding and control of these phenomena, a multi-faceted theoretical approach is employed in this project, consisting of: (i) The investigation of relatively unexplored regimes with the potential to unveil novel behaviors – in particular, the study of competing phases taken out of equilibrium to explore the potential to enhance the transition temperatures of unconventional superconductors by optical pulses. (ii) The embracement of realistic features of correlated materials in their microscopic descriptions – in particular, the investigation of the impact that disorder, in its various forms, has on electronic smectic and nematic states present in the phase diagrams of unconventional superconductors. (iii) The promotion of synergy with established and novel experimental probes, with particular emphasis on scanning tunneling microscopy and ultrafast spectroscopy, not only by using data as input of theoretical models, but also by providing concrete guidance for experiments.

FY 2014 HIGHLIGHTS

Funding for this project was initiated in mid-July, 2014. Since then, we have made important progress on the impact of disorder to the unconventional superconducting state promoted by quantum critical fluctuations, and also on the behavior of the nematic degrees of freedom in iron-based superconductors in the presence of impurities. We have also been developing a framework to extract impurity potentials from scanning tunneling microscopy data. Its initial application to dichalcogenide charge-ordered superconductors revealed that the charge density-wave instability in NbSe₂ is promoted not by Fermi surface nesting, but rather by the coupling to soft phonon modes.

Theoretical Description of Pump-Probe Experiments in Ordered Materials

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Funding: \$360,000 (2014-2016)

PROGRAM SCOPE

The Department of Energy has a significant investment in large equipment that can generate state-of-the-art ultrashort pulses from free-electron lasers like the Linac Coherent Light Source (LCLS). This has led to a series of new ultrafast pump-probe experiments to try to measure the dynamics of strongly correlated materials. Many of these experiments have been performed on materials in ordered phases, such as charge density wave (CDW) materials or superconductors (SC). We have been performing research in this field for some time now, and in this project, we plan to expand our efforts from primarily working in the normal state, to working in the ordered phases of these materials. We will extend our theoretical calculations to include the effects of the ordered phases, investigating electron-phonon coupled materials that order in a CDW or SC phase. We will examine an interesting type of quantum critical point that is seen a strongly correlated CDW phase, which involves a transition from an insulator to a metallic CDW as a function of temperature, with the metallic phase separating a weakly correlated CDW insulator from a strongly correlated insulator at $T = 0$. Finally, we will work to develop the theoretical description of novel pump-probe experiments like time-resolved electronic Raman

scattering. We will also apply these techniques to models of real materials like graphene and the CDW-ordered material 1T-TaS₂. Our project will be applying recent advances in nonequilibrium many-body physics to experiments of high interest to the Department of Energy (DOE) and represents a significant scientific challenge which is in the area of materials driven far from equilibrium (one of the DOE challenge areas).

FY 2014 HIGHLIGHTS

During the past year, we completed a significant amount of research on the nonequilibrium behavior of the simplest charge-density-wave insulator. We examined time-resolved photoemission, dielectric breakdown, high harmonic generation, and the quantum excitation process. In addition, we completed much work on electron-phonon coupled systems, including situations when the system is in a superconducting state. This includes deriving sum rules for the Green's functions and self-energies even in the presence of external fields, and examining the relaxation pathways and the spectral weight redistribution that one would see in a time-resolved photoemission study. Finally, we corrected and resubmitted a manuscript on time-resolved photoemission in graphene. We also spent time working on universal properties of bad metals by invoking an extremely simple model for the transport density of states and showing that it naturally leads to a linear resistivity at moderate temperature and that it leads to a universal behavior of the thermopower, which is captured qualitatively by the simple Kelvin formula for the thermopower. We have a number of projects underway, which include generalizing the CDW work to models that have many-body interactions and expanding the electron-phonon coupling work to include a renormalization of the phonon bath due to heating by the electrons.

EARLY CAREER: Predictive Theory of Topological States of Matter

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Funding: \$150,000 (2014)

PROGRAM SCOPE

The goal of this project is to develop a theory of new topological states of matter and predict their material realizations. The PI has mainly focused on topological states protected by crystal symmetries, which he terms 'topological crystalline insulators'. Specifically the PI aims to 1) develop a systematic approach to classify topological phases that exhibit robust surface or edge states, within the framework of band theory of periodic solids, 2) identify their material realizations, predict experimentally testable signatures and propose device applications of topological materials, 3) develop a theory of topological phase transitions in the presence of disorder and/or interaction, and 4) study the rich interplay between topological order and symmetry breaking. Results from this project will significantly expand the horizon of topological matters, offer unique insight into the competition between localization and itinerancy in correlated electron systems, and pave the way for applications in tunable electronics and fault-tolerant quantum computation.

FY 2014 HIGHLIGHTS

(1) In collaboration with Vidya Madhavan's STM group, the PI discovered Dirac mass generation from ferroelectric structural distortion in the topological crystalline insulator (TCI) PbSnSe, which spontaneously and partially breaks the underlying crystal symmetry. This work reveals the first example of a topological system that is highly tunable by symmetry breaking, and unambiguously demonstrates how symmetry protects topological order. Publication: Science 341, 6153 (2013) (2) The PI's group (with Jagadeesh Moodera) proposed the concept of topological field effect transistor based on a two-dimensional topological crystalline insulator, as realized in SnTe thin films. The working mechanism of the proposed device relies on the unique properties of TCI conducting edge states, i.e., applying a vertical electric field opens up a gap and hence shuts off the conduction. Publication: Nature Materials 13, 178 (2014) (3) The PI (with a graduate student Evelyn Tang) found that strain has a dramatic effect on topological crystalline insulator surface states: it creates a pseudo-magnetic field as large as 200T and leads to the formation of Landau levels while maintaining time-reversal symmetry. The PI proposed that these Landau levels could be responsible for interface superconductivity that has been observed (but not understood) in IV-VI semiconductor heterostructures. Publication: Nature Physics 10, 964-969 (2014) (4) The PI's group predicted a new class of topological crystalline insulators in anti-perovskites with chemical formula A_3BO . Experimental groups are currently working to search for the predicted topological surface states. Publication: PRB, 90, 81112 (2014).

Theory of Fluctuations in Superconductors

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Funding: \$103,000 (2014)

PROGRAM SCOPE

The general objective of the DOE project is to explore fluctuation phenomena and related strong-correlation physics in a wide variety of interacting material systems, including superconductors, heavy-fermion materials, topological insulators, and magnetic systems. Specifically, the following research projects are being undertaken and explored: 1. Interplay between topological superconductivity and odd-frequency pairing in superconducting proximity systems and specifically, the role of disorder and fluctuations in these topological heterostructures; 2. Fluctuations and strong-correlation effects in topological Kondo insulators and superconductors; The former have been predicted by the PI and recently discovered experimentally in Samarium hexaboride. One of the important fundamental, open problems is to understand the effect of strong interactions and Kondo fluctuations on the topological surface states, and possible magnetic phase transitions on the surface of these materials. 3. Development of non-perturbative theoretical methods to describe quantum dynamics in fluctuating superconductors, in particular, properties of possible quantum soliton excitations in superconducting/superfluid phases; Soliton dynamics. 4. Understanding Casimir effect (interaction between macroscopic and mesoscopic systems mediated by quantum fluctuations of electromagnetic field) between interacting electron systems; Casimir effect across thermal and quantum phase transitions. Tunable Casimir repulsion between topological states of matter.

FY 2014 HIGHLIGHTS

(1) A theory of proximity effect from a topological superconductor into a disordered metal has been developed [Phys. Rev. B 89, 174521 (2014) and arXiv:1408.4395]. A key new, surprising result is that proximity-induced unconventional superconductivity remains relatively long-ranged and is not suppressed by disorder as strongly as previously believed. This result has important implications for the ongoing experiments on topological superconductor/semiconductor heterostructures. (2) An exact description of a moving soliton in a one-dimensional superconductor has been derived. The exact solution includes an exact soliton spectrum (previously unknown) and effective mass of the soliton. (3) In a series of works [Phys. Rev. B 90, 081113 (2014), Phys. Rev. B 90, 155314 (2014), arXiv:1410.1868], the PI developed a theory of fluctuations in topological Kondo insulators (TKIs) – a new class of strongly-correlated topological insulator, predicted by the PI. A key new result is the occurrence of a magnetic phase transition on the surface of TKIs. (4) A non-perturbative (asymptotically exact) theory of a strongly-correlated one-dimensional TKIs has been developed in preprint, arXiv:1411.5357 (5) In Phys. Rev. B 90, 075420 (2014), the PI proposes a new line of research where the well known Casimir effect (interaction between macroscopic bodies mediated by quantum fluctuations of the electromagnetic field) could be used to probe the internal structure and transitions in low-dimensional materials experiencing the Casimir forces. (6) A theory of tunable repulsive Casimir effect between Weyl semimetals has been developed. (7) In a theory-experiment collaborative paper with the Z. Hasan group at Princeton (under review in Nature Physics), the PI developed a qualitative theory of photoinduced giant surface life-time of an intrinsic topological insulator.

Semiconductor Nanostructures by Scientific Design

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Funding: \$470,000 (2014)

PROGRAM SCOPE

We continued our research on opto-electronic properties of semiconductor nanoparticles on two fronts: (i) method developments and (ii) applications to systems of interest for solar energy conversion. We also extended our investigations to nanostructured solids. On the front of method developments we completed the writing of a code (WEST) for large scale GW calculations [1] and we carried out a systematic analysis [2] of the approximations involved in the solution of the Bethe-Salpeter equation (BSE) based on density functional perturbation theory. On the front of applications, we focused on blinking of isolated Si nanoparticles (NPs) [3] and on multi-exciton generation (MEG) in Ge nanoparticles [4], and on nanostructured Si clathrates [5].

FY 2014 HIGHLIGHTS

1. Absorption and emission spectra from first principles: theoretical improvements: (i) We carried out a parallel implementation of the algorithm previously developed for GW calculations, which takes advantage of separable expressions of both the single particle Green's function and the screened Coulomb interaction and we applied it to systems of unprecedented size (thousands of electrons). (ii)

We systematically studied BSE spectra in Si nanoparticles. 2. Study of nanoparticles and nanostructured solids for solar energy conversion: clathrates, perovskites, and Si and Ge nanoparticles.

Non-Equilibrium Effects in Quantum Coherent Superconducting Nanostructures

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Funding: \$175,000 (2014)

PROGRAM SCOPE

Quantum coherent superconducting circuits are key elements of promising qubit prototypes, the building blocks of a quantum computer. Recent years has witnessed a fast progress in design of nanostructures and in probing their dynamics with time-resolved measurements in the microwave frequency range. These developments call for deeper theoretical understanding of collective modes in model superconducting circuits such as long Josephson junctions arrays, superconducting point contacts, and nanowires. An important subject is the coherence time of such collective modes, fundamentally limited by their interactions with quasiparticles. The present proposal aims at filling the exposed gaps in the theoretical understanding of these issues and at facilitating further development of experimental and theoretical physics of coherent superconducting circuits. Specifically, the aims of this project are: (1) developing a theory of spectra and relaxation of collective modes in long Josephson junctions arrays with quantum-coherent dynamics of the order parameter; (2) elucidating effects of the charge disorder on the dynamics of such arrays; (3) developing a theory of relaxation of the chemical potential imbalance between one-dimensional quasi-condensates coupled by Josephson tunneling; (4) investigating damping of quantum oscillations of the order parameter in superconducting nanobridges and point contacts induced by quasiparticle excitations; (5) addressing large non-equilibrium fluctuations of the superconducting order parameter of a DC-current-biased nanowire discovered in recent experiments. The success of the project will contribute to a deeper understanding of the fundamental properties of quantum coherent superconducting devices. Most of the anticipated results are of immediate interest for a number of experimental groups.

FY 2014 HIGHLIGHTS

In this funding period, we (1) built a theory which ultimately helped to resolve a long-standing puzzle in the physics of Josephson effect, (2) explained the experimentally-observed switching between the superconducting and normal state of a nanowire, (3) developed a dynamical theory of Majorana states in a topological Josephson junction, (4) extended the theory of antiferromagnetic exchange between magnetic impurities in a superconducting host, and (5) proposed a new collective state of interacting bosonic particles having a degenerate spectrum. In the theory of Josephson effect, we related the energy relaxation time of a qubit to the dissipative part of the Josephson current. That enabled, for the first time in 50 years since the seminal Josephson's publication, a precision measurement of the dissipative part of the Josephson current. Our dynamical theory of Majorana states set limits for the prospects to detect these states by means of measuring Shapiro steps in current-voltage characteristics of a topological Josephson junction. The theory of antiferromagnetic exchange which we developed, accounts for the formation of localized states (so-called Shiba states) associated with the magnetic

impurities in superconductors. This extension of theory is important for designing ways of engineering p-wave superconductors from readily available elements. The results of our research were published in nine papers, including articles in Nature, Nature Physics, Applied Physics Letters, and four publications in Physical Review Letters.

EARLY CAREER: Simulation of Correlated Lattice and Impurity Systems Out of Equilibrium

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Sr. Investigator(s):
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Funding: \$150,000 (2014)

PROGRAM SCOPE

Correlated quantum systems out of equilibrium exhibit a wealth of intriguing and unexpected quantum phenomena. Our theoretical understanding of these phenomena lags far behind our experimental capabilities, as standard analytic approaches routinely fail and a solution of the quantum mechanical equations of motion precise enough to describe correlation physics is not available. In this project I propose to develop unbiased and numerically exact methods for numerically simulating correlated quantum impurity and lattice models out of equilibrium, based on continuous-time quantum Monte Carlo algorithms. We will use these methods to systematically study the physics of correlated quantum systems in non-equilibrium situations.

FY 2014 HIGHLIGHTS

2014 allowed us to analyze the behavior of impurity systems in steady state, e.g. with a voltage applied, and thereby allowed us to examine the voltage splitting of the Kondo peak with numerically exact methods.

High Performance First-Principles Molecular Dynamics for Predictive Theory and Modeling

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Eric Schwegler; Lawrence Livermore National Laboratory
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Funding: \$633,963 (2014)

PROGRAM SCOPE

This project aims to develop high-performance software tools for First-Principles Molecular Dynamics (FPMD) simulations, and apply them in investigations of materials relevant to energy conversion processes. FPMD is an atomistic simulation method that combines a quantum-mechanical description of electronic structure with the statistical description provided by molecular dynamics (MD) simulations. This reliance on fundamental principles allows FPMD simulations to provide a consistent description of

structural, dynamical and electronic properties of a material. This is particularly useful in systems for which reliable empirical models are lacking. FPMD simulations are increasingly used as a predictive tool for applications such as batteries, solar energy conversion, light-emitting devices, high-K dielectric materials and phase-change materials for optical storage devices. The accuracy and predictive power of FPMD comes at the price of a high computational cost. Simulations of systems including a few hundred atoms require high-performance computers and parallel programs. This project addresses the issues of extending the size of systems that can be simulated, improving the accuracy of the electronic structure calculations underlying FPMD simulations, and increasing the efficiency of sampling methods beyond the conventional molecular dynamics approach. Furthermore, we are developing new algorithms for the computation of spectroscopic data, such as Raman and infrared spectra. The computation of these quantities during a simulation allows for a direct comparison with experimentally measured optical and vibrational spectra. These new algorithms are implemented in high-performance simulation codes that run on the ANL BlueGene/Q Leadership-class computer. They are currently applied to simulations of liquids, aqueous solutions, and solid/water interfaces relevant to electro-chemical energy conversion devices.

FY 2014 HIGHLIGHTS

We redesigned numerically intensive parts of the Qbox code to improve scalability on the BlueGene/Q platform, enabling FPMD simulations of a 4096-atom silicon carbide (SiC) sample (16384 electrons) and static electronic structure calculations of a 12288-atom SiC sample (49152 electrons) on 524288 cores of ANL Mira. We developed scalable algorithms for electronic structure computations using accurate hybrid density functionals, combining a random search for an optimal distribution of orbitals, and a replication of orbitals among processors. This enabled PBE0 calculations of the electronic ground state of a 4096-atom SiC sample (16384 electrons) on ANL Mira (BlueGene/Q) using 32k cores, with 6400s / SCF iteration. We implemented calculations of electric polarization and polarizability in Qbox, enabling simulations of infrared and Raman spectra, respectively. We carried out the first *ab initio* simulations of the Raman spectra of liquid water by combining FPMD and density functional perturbation theory, showing the importance of electronic effects in the interpretation of Raman spectra. We simulated the IR spectrum of water at the alumina (0001)/water interface. We carried out the first *ab initio* calculation of the absolute position of the band edges in liquid water using the GW approximation, an essential step toward the prediction of water redox potentials w.r.t. band edges of semiconductors and insulators. We carried out PBE0 simulations of a dilute NaCl aqueous solution, showing that changes of the water structure are mostly localized in the ion's first solvation shell. We implemented rare-event sampling methods using a client-server model in Qbox, coupling a DFT calculation with a driver program that implements an arbitrary sampling algorithm. Simulations of liquid water using replica-exchange molecular dynamics between 200 K and 600 K allowed for direct comparisons of the sampling efficiency with traditional FPMD simulations.

Quantum Quench Dynamics-Crossover Phenomena in Non-Equilibrium Correlated Quantum Systems

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Funding: \$300,000 (2014-2016)

PROGRAM SCOPE

We are developing tools to analyze crossover phenomena in the transient dynamics of closed quantum systems, using boundary conformal field theory, integrability, and numerical diagonalization. Studying for instance the real-time evolution of the Loschmidt echo and the work distribution function in quantum impurity systems, we are able to determine the characteristic crossover time, energy and spatial scales (as well as the full scaling functions) related to the Kondo coupling and to the electron interactions in the Hamiltonian. This, in turn, provides powerful methods to investigate the physics of these systems, both theoretically and experimentally. Currently, we are working our way towards the transient dynamics of open quantum systems by studying disordered quantum spin systems from the quenched to the annealed limit, finally considering the case of a fully fluctuating environment.

FY 2014 HIGHLIGHTS

We developed a framework to tackle local quantum quenches in integrable impurity systems, combining a mapping onto a boundary problem with the form factor approach to boundary-condition-changing operators. We showed how to compute exactly the Loschmidt echo and the distribution of the work done during the quantum quench. Our results display an interesting crossover physics characterized by the energy scale of the impurity corresponding to the Kondo temperature. We discussed in detail the non-interacting case as a paradigm and benchmark for more complicated integrable impurity models, and checked our results using numerical methods. The calculated time evolution of the Loschmidt echo was found to be in beautiful agreement with independent numerical studies of an equivalent lattice model. Applying the same formalism to the Kondo case is a bit more involved, since the form factors are more complicated in this case. However, the problem is not fundamentally different from the case treated in the preprint, the physics of the quenches being essentially interacting in that case as well. We also studied crossovers in quantum impurity problems from the point of view of entanglement entropy. This is a potentially very rich direction of research, as the entanglement might provide an alternative way to study subtle correlation phenomena such as the screening cloud, and might also exhibit, in out of equilibrium set-ups, deep relations with the full counting statistics. In this context however, the entanglement is particularly difficult to study since the methods of conformal invariance cannot be applied. We established that the entanglement is a non-perturbative quantity at small coupling, but that it can be approached perturbatively at strong coupling in the Kondo and resonant level model cases by using the underlying integrability. Finally, we developed a variant of the foregoing form factors approach to calculate the entanglement non-perturbatively.

Theory of Electron Imaging in Small Devices

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

We are entering a new golden era of condensed matter physics with practical applications to devices. The combination of qualitatively new electronic materials (like graphene), atomic scale experiments

going on around the world, the level of interest in theoretical understanding and support of experiments the highest it's ever been, backed by the most powerful computers we ever had, have made this golden age possible. Our expertise and this project pertain to the two-dimensional electron flow in semiconductors, an essential component of this new research horizon. Although we have already made significant progress in this area, much remains to be learned about how to control the flow of electrons, what exactly it is microscopically, and how to exploit some of its unusual properties of new materials in creative ways to make devices, especially very fast and efficient devices.

FY 2014 HIGHLIGHTS

In 2014 we have completed work on quantum optimal control theory to demonstrate high-fidelity coherent control of electronic charge in semiconductor double quantum dots. We continued work on magnetoconductance that indicates fractal scaling. In the calculations of the fractality we used detrended fluctuation analysis—a widely used method in time-series analysis—and show its usefulness in the interpretation of the conductance curves. We continued work on branched electron flow and made several new discoveries to be published. In addition, we started a new line of work on spectroscopy of graphene and related carbon nanosystems that promises a far better idea of the factors controlling the spectroscopy than found in the existing literature.

EARLY CAREER: New States of Matter and Quantum Simulation with Ultracold Alkaline Earth Fermions

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Funding: \$150,000 (2014)

PROGRAM SCOPE

A major goal of condensed matter physics is the identification and characterization of new states of matter. Strongly correlated quantum systems, in which interactions among the constituents play a crucial role and lead to numerous incompletely understood phenomena, provide a fruitful setting to pursue this goal. This project aims in part to explore new parameter regimes of strongly correlated quantum systems, in part to help identify promising candidate systems for new states of matter. Current and recent efforts focus on two classes of systems: (1) Ultracold fermionic alkaline earth atoms (AEA) in optical lattices: The primary interest in these systems stems from the fact that ultra-cold AEA can have large nuclear spins (up to $I=9/2$) with $J=0$. As a result, to an excellent approximation, a very large $SU(N)$ spin symmetry ($N = 2I+1$) is present. Earlier work of the PI and collaborators pointed out similarities between these systems and more familiar $SU(2)$ frustrated magnets, highlighting the potential richness of condensed matter phenomena in ultra-cold AEA. (2) Correlated electron systems with strong spin-orbit coupling: These systems include iridates and other 5d transition metal oxides, as well as f-electron materials. Such systems are characterized by interplay between strong spin-orbit coupling and substantial electron correlation. This leads to novel magnetic and electronic degrees of freedom that provide a new set of microscopic building blocks, potentially leading to topological and other new states of matter. In addition, this project also aims to advance the understanding of the role of symmetry in quantum phases of matter, with a particular focus on topological phases of matter. Goals include

building bridges between powerful but abstract classifications and physical properties, and understanding constraints imposed by general principles on properties of such phases.

FY 2014 HIGHLIGHTS

1. In $A_2B_2O_7$ pyrochlores, we observed that strong spin-orbit coupling can lead to a novel type of Kramers doublet for which the Kramers pseudospin is time-reversal odd (as it must be), but does not transform like a magnetic dipole under space group. Instead, the pseudospin has mixed dipolar-octupolar character. This is distinct from the $j_{\text{eff}}=1/2$ doublets that occur in iridates, which have dipolar pseudospin. We showed that dipolar-octupolar (DO) doublets can occur for $5d^1$, $5d^3$ and various $4f$ ions with D_{3d} site symmetry, for instance both the A and B sites in the pyrochlore structure. In fact, there is evidence DO doublets occur for the f-moments in A=Nd, Dy pyrochlores. We showed that the most general symmetry-allowed spin exchange Hamiltonian for DO doublets on the pyrochlore lattice is the surprisingly simple spin-1/2 XYZ model. This model supports two distinct quantum spin ice phases, one of which is a novel “octupolar” quantum spin ice that we identified for the first time. This work was published as: Y.-P. Huang, G. Chen and M. Hermele, Phys. Rev. Lett. 112, 167203 (2014). Inspired by our work, Melko and co-workers found evidence via quantum Monte Carlo simulation for a Z_2 spin liquid phase dubbed “quantum kagome ice,” in a model of DO doublets on the kagome lattice (1407.0037). 2. We collaborated with the Dessau group (angle resolved photoemission spectroscopy experiment) at Boulder, focusing on understanding the effect of Rh doping in $Sr_2Ir_{1-x}Rh_xO_4$. In particular, we proposed a simple mechanism by which Rh doping may lead to the observed hole doping of the Ir 5d states. This work is currently available as arXiv:1406.4978 and is being submitted for publication. 3. We devised and tested a method for detecting crystal symmetry fractionalization from ground state wavefunctions, in certain topological phases. This work was in collaboration with Andrew Essin, Ling Wang and Olexei Motrunich, and is available at arXiv:1409.7013 and is under consideration for publication.

SciDAC Partnership: Predictive Computing for Condensed Matter

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Shinsei Ryu; Illinois-Urbana Champaign, University of
Lucas Wagner; Illinois-Urbana Champaign, University of
Garnet Chan; Princeton University
Shiwei Zhang; William and Mary, College of
Students: 4 Postdoctoral Fellow(s), 9 Graduate(s), 3 Undergraduate(s)
Funding: \$689,999 (2014)

PROGRAM SCOPE

Vision: We aim at establishing general and predictive mathematical theories for solids and computational methods that implement them. We will then apply these methods to outstanding solid-state problems, with a view to solving them computationally. Theories: We will develop electronic structure theories for solids that are predictive in the sense that the fidelity of simulation can be increased systematically; that can handle excited electronic states and thus response properties; that

can be applied to strongly correlated electronic structures by exposing hidden mathematical structures and symmetries therein. To achieve this, we will extend systematic diagrammatic many-body methods to solids in ground and excited states at zero and nonzero temperatures with pristine and doped states. We will implement them in parallel software, utilizing highly scalable Monte Carlo algorithms. We will also fully develop and apply quantum Monte Carlo (QMC) methods for solids including those with strong correlation. We will furthermore explore emerging, novel, systematic mathematical theories and computational methods for strongly correlated solids including density matrix renormalization group, dynamical mean-field theory, and Slater-determinant-based QMC including auxiliary-field QMC, full configuration-interaction QMC, and more. Software: We will create a suite of software implementing the aforementioned predictive electronic structure theories for solids, which are, by virtue of exploiting novel algorithms, scalable with respect to both problem size and computer size. Applications: We will apply the predictive methods as implemented in massively parallel software to some of the most outstanding condensed matter problems, including unexplained experimental results. Our target problems include cuprate high- T_c superconductivity, structures of molecular crystals, excited states in solids, Peierls transitions in Luttinger liquids, and 2D Mott–Hubbard insulators.

FY 2014 HIGHLIGHTS

We have published or submitted 32 papers and book chapter in journals such as Science, Nat. Commun., and J. Chem. Phys. We made a large stride toward our understanding of the high- T_c superconductivity in cuprates by performing realistic, accurate, and massively parallel QMC calculations of three cuprate materials. They revealed the strong coupling of magnetic and lattice degrees of freedom present in these materials. We invented three novel, scalable stochastic methods that can compute excited states of molecules or solids by combining many-electron theories with Monte Carlo algorithms. The most fully developed among these is the auxiliary-field QMC method with an appropriate constraint on its auxiliary field to remain excited-state-like, which can thus calculate the quasiparticle energy bands of solids. The second is the full configuration interaction QMC method with a modified propagator, which can yield not only excited-state energies of a molecule but also its density of states. The third combines *ab initio* many-body perturbation theories with Monte Carlo integrations to calculate directly the correlation energies and quasiparticle energy bands of solids without the fermion sign problem. We lead the development of quantum metrics for strong correlation. Entanglement entropy classifies topological insulators and superconductors and is one of the most important concepts in quantum critical systems. We extended this concept to a broader class of tensor network wave functions such as the Multiscale Entanglement Renormalization Ansatz (MERA). We developed new methods for strong correlation. We combined Density Matrix Renormalization Group (DMRG) and QMC to arrive at a scheme for strong correlation with accuracy unachievable with either method alone. We developed density matrix embedding theory for strong correlation. We pioneered the use of symmetry-projected Hartree-Fock wave functions as an auxiliary field QMC (AFQMC) method, improving both accuracy and efficiency. We performed *ab initio* calculations of a benzene crystal and a phase transition in solid CO_2 .

Theory of Novel Superconductors

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Funding: \$315,000 (2014-2016)

PROGRAM SCOPE

The research in this program is devoted to a series of problems related to electron pairing, magnetism, and disorder in unconventional superconductors. Studies are directed towards understanding the microscopic mechanism of Fe-based and other novel superconductors, and developing quantitative and even predictive methods. The optimal materials for high-temperature superconductivity almost certainly represent a set of measure zero in the space of all possible materials. Finding them by conventional experience-based methods has proven frustrating. Working with collaborators in the *ab initio* community, we aim to develop computational methods to guide the search for new superconductors, focusing on unconventional pairing mediated by electronic excitations treated within the fluctuation exchange approximation. The goal will not be a quantitative predictor of the critical temperature T_c for a given material, but an understanding of how crystal structure, Fermi surface electron orbital character, and local interactions influence it. Research performed in collaboration with Prof. Roser Valenti at U. Frankfurt and her group.

FY 2014 HIGHLIGHTS

(1) Spin fluctuation theory in Fe-based superconductors. With R. Valenti DFT group, we studied pairing by spin fluctuations in Fe chalcogenide systems, in particular trying to understand the pressure dependence of T_c . Empirically it is known that applying approximately 10 GPa raises the T_c of FeSe from 8K to about 30K, but other Fe-based materials have very different pressure dependences. We found that FeSe is quite an unusual material, in that several magnetic states compete and lead to magnetically frustrated ground state; pressure dependence of T_c is due to the rapid suppression of pairbreaking fluctuations with pressure (ms. in preparation). We also studied intercalated FeSe systems, and showed how to understand the effect of layer separation and doping on T_c (arXiv:1410.7565). Finally, we investigated the effect of glide plane symmetry in Fe-based superconductors and the possibility of eta-pairing (arXiv:1411.0070) (2) Phenomenological theories of disorder in Fe-based superconductors. In the past year we have developed a strong collaboration with R. Prozorov at Ames and T. Shibauchi at Kyoto who are both making measurements of electron irradiation at the Irradiated Solids Lab in Paris. We compared with T_c suppression and penetration depth measurements on a number of samples. (Nat. Comm. 5, 5657 (2014); Phys. Rev. X 4, 041032 (2014)) We also performed 5-band Bogoliubov deGennes calculations of impurity bound states with Brian Andersen at Niels Bohr Institute. (Phys. Rev. B 88, 220509 (2013); *ibid*, 90, 134520 (2014); arXiv:1407.1846)

Theory of Topological Quantum Numbers in Low Dimensions

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Funding: \$125,000 (2014)

PROGRAM SCOPE

Many remarkable phenomena in two dimensions, such as the fractional quantum Hall effect (FQHE), topological insulators, anomalous quantum spin Hall effect, Majorana modes and Chern insulators, have topological underpinnings. A general topological classification serves as a useful guide but does not tell

us under what conditions the states would occur, and what interesting properties of these states go beyond topology. My goal has been to investigate the experimental realizability of various topological states of matter. This has required detailed microscopic calculations, as well as close collaboration with experimental colleagues. The topics of interest include the physics at the edge of a FQHE state, rapidly rotating ultra-cold atoms, signature of fractional braid statistics, FQHE of composite fermions and of two-component bosons. We have made progress on some of these topics. In collaboration with experimental colleagues at Columbia, we have identified a small skyrmion in the excitation spectrum in the vicinity of the $1/3$ state. In collaboration with experimental colleagues at Princeton, we have shown that spin phase transitions are a very sensitive probe of the effect of Landau level mixing. We have also performed theoretical calculations that show that the edge of the $5/2$ FQHE is 'reconstructed' for the experimental parameters. Our current research focuses on certain concrete ideas that we believe should make a direct observation of fractional statistics possible in rotating cold atom systems. In addition, we are exploring the possibility of creating a Fermi liquid metal in a system of interacting bosons in two dimensions. We are also in the process of creating a comprehensive catalog of all FQHE states that we can envision at the moment for multi-component systems, which should be very useful for the analysis of FQHE experiments in graphene as well as for identifying new phenomena.

FY 2014 HIGHLIGHTS

The articles supported by the DOE grant are listed below. Some of the summaries are as follows: In paper 3 we have shown that certain states, such as those occurring at $4/11$ and $5/13$, have an origin different from all other fractional states. In paper 6 we have shown that the partially polarized fractional quantum Hall state at $3/8$ is, theoretically, an exact representation of a chiral p-wave pairing. In 6 we have proposed a way to measure fractional braid statistics in cold atom systems, where it appears as fractional angular momentum. [1] A note contrasting two microscopic theories of the FQHE, J. K. Jain, Indian J. Phys., DOI 10.1007/s12648-014-0491-9 (2014). [2] Collective excitations of a system of coupled relativistic and non-relativistic two-dimensional electron gases, Ajit C. Balram, Jimmy A. Hutasoit, Jainendra K. Jain, Phys. Rev. B 90, 045103 (2014). [3] Enigmatic $4/11$ state: A prototype for unconventional fractional quantum Hall effect, S. Mukherjee, S. S. Mandal, Y. H. Wu, A. Wojs, and J. K. Jain, Phys. Rev. Lett. 112, 016801 (2014). [4] Spin polarization of composite fermions and particle-hole symmetry breaking, Y. Liu, S. Hasdemir, A. Wojs, J. K. Jain, L. N. Pfeiffer, K. W. West, K. W. Baldwin, M. Shayegan, Phys. Rev. B 90, 085301 (2014). [5] Possible realization of a chiral p-wave paired state in a two-component system, S. Mukherjee, J. K. Jain, and S. S. Mandal, Phys. Rev. B 90, 121305 (2014). [6] Fractional angular momentum in cold atom systems, Y. Zhang, G. J. Sreejith, N. D. Gemelke, and J. K. Jain, Phys. Rev. Lett. 113, 160404 (2014). [7] Long-range spin-triplet helix in proximity induced superconductivity in spin-orbit-coupled systems, X. Liu, J. K. Jain and C. X. Liu, Phys. Rev. Lett. 113, 227002 (2014). [8] Single-Fluxon controlled resistance switching in centimeter-long superconducting gallium-indium eutectic nanowires, W. Zhao *et al.*, Nanoletters, doi: 10.102/nl503283e (2014).

EARLY CAREER: Emergence of High T_c Superconductivity out of Charge and Spin Ordered Phases

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 Sr. Investigator(s):
 Students: 1 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
 Funding: \$150,000 (2014)

PROGRAM SCOPE

We will study mechanisms and roles of charge/spin orders in two classes of high T_c superconductors: (1) Cuprates and (2) Fe-based superconductors. For cuprates the PI played a central role in identifying one of the new charge ordered phases in the cuprates: intra-unit-cell (IUC) nematic and its coupling to stripe dislocations. We will build on this experience to pursue associated quantum phase transitions in collaboration with Davis group, while seeking microscopic understanding of the roles IUC nematic and smectic play in superconductivity. For Fe-based superconductors, we will develop new ways to analyze scanning tunneling spectroscopy (STS) data to probe electron-collective mode coupling and test their role in superconductivity. Through parallel efforts in the two chemically distinct HTSC's exhibiting tantalizingly similar phase diagrams, we will seek more broadly applicable organizing principles. We will take a symmetry-guided "middle-up/down approach": applying symmetry and quantum field theory based perspective to experimental data and using the results as input to microscopic models. The coexistence or proximity between charge and spin order and superconductivity occur in a region where interaction energy is comparable to kinetic energy. While the resulting complexity in the electronic phase diagram is an important problem in the modern materials research, the uncertainty principal inhibits a single sweep numerical solution of relevant fermionic hamiltonians. The PI and collaborators have proven through the discovery of IUC nematic that a middle-up/down approach can be very effective. We will extend the scope of the approach to include various numerical techniques through collaborations with experts. The combination of the theoretical expertise of the PI in this field, and synergetic interactions with Davis group (STS) at Cornell puts her in a position to make unique contributions that can impact both theory and experiments.

FY 2014 HIGHLIGHTS

[1] Direct phase-sensitive identification of a d-form factor density wave in underdoped cuprates. Proceedings of the National Academy of Sciences of the USA 111, E3026-E3032 (Jul 2014). [2] Nematic and spin-charge orders driven by hole-doping a charge-transfer insulator. New J. Phys. 16 093057 (2014). [3] Identifying the 'Fingerprint' of Antiferromagnetic Spin-Fluctuations on Iron-Pnictide Superconductivity. <http://www.nature.com/nphys/journal/vaop/ncurrent/full/nphys3187.html>. doi:10.1038/nphys3187.

Correlation Effects and Magnetism in Actinides: Elements and Compounds

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Funding: \$150,000 (2014)

PROGRAM SCOPE

The objective of our research is to achieve a fundamental understanding of the solid state phases of materials containing elements from the actinide series. To reach this goal we will construct computational electronic structure tools based on extensions of the Dynamical Mean Field Theory (DMFT) such as LDA+DMFT to carry out first principles calculations of these correlated materials. In addition we develop simplified physical pictures and phenomenological models of the various phases of

these elements and their electronic structure which in turn can be used to predict new experiments. Building on the advances of the previous funding period, we will focus on the magnetic properties of the actinides. We will elucidate the physical principles that govern the formation of local moments of the 5f electrons, their quenching in non-magnetic materials and their possible magnetic long range order phases. We will use LDA+DMFT to compute the spectrum of the spin fluctuations of delta Pu. We will extend our previous structural studies to complex structures such as the alpha phase, and develop faster algorithms to evaluate its total energy as a function of volume.

FY 2014 HIGHLIGHTS

Predicted the inelastic neutron scattering cross section of delta Pu, and validated the theoretical approach against experimental results from LANL.

Toward High-Accuracy Point Defects Calculations in Materials

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Funding: \$135,000 (2014)

PROGRAM SCOPE

The goal of the project is to improve our understanding of point defects in materials, in particular systems with strong correlations, and electron-phonon coupling, such as oxides. The project initially was geared toward the development and testing of new methods to incorporate self-energy effects (as obtained in the quasiparticle self-consistent (QS)GW) method for the host system in larger cell defect calculations by using a real space representation of the self-energy expanded in muffin-tin orbitals and/or a related LDA+U approach. In the process of studying particular systems, new directions evolved leading to a new focus, namely to explore how phonons contribute to the dielectric screening and how this enters into different aspects of electronic structure, for example GW self-energy, exciton binding energy, and self-trapped polaron formation. Several aspects of this overall focus of the project were pursued in different materials systems, including ZnO, V_2O_5 , halide perovskites, oxide perovskites, transition metal dichalcogenides and rare-earth nitrides. In terms of point defects, an important test case considered was N_2 on the Zn-site in ZnO. It was proposed by us as a possible candidate for explaining a N-related shallow level in ZnO and shown to be related to a known electron paramagnetic resonance (EPR) center. Further work is on-going on this topic to study alternative N-involving complexes, such as V_{Zn}^{-NO} and to further confirm the proposed model by explicit calculations of the EPR g-factors and hyperfine factors. The effects of strain on the band structure and in particular spin-orbit splittings were investigated in MoS_2 and graphene. Another layered material, V_2O_5 , was explored, as an ultrathin (monolayer) material and found to present extreme challenges in terms of understanding lattice polarization effects on the band structure. Halide perovskites, a new promising family of solar cell materials were explored in terms of phonons and electronic band structure and their interactions.

FY 2014 HIGHLIGHTS

1) We collaborated with Mark van Schilgarde at King's College, London, UK to explore the possibilities of a real space representation of the QSGW self-energy in an Imto basis set for defect calculations. The code manipulating the self-energy and adapting it from one system to another was mainly developed by him and is now ready to be tested in various defect situations. On the other hand, we have continued our previous approach of adapting U parameters of LDA+U to QSGW band structures to then study defects in LDA+U. This was applied to the problem of the oxygen vacancy in LaAlO_3 and to the study of self-trapped polarons. These studies are still in initial stages. 2) We continued our study of V_2O_5 . While in the first year the focus was on understanding the phonon differences in bulk and monolayer, we now carried out QSGW band structure calculations and found QSGW to overestimate the gap much more than usual. The solution to this problem appears to be the inclusion of lattice vibration effects on the long-range polarization which in turn affects the screening of the Coulomb interaction W entering the GW approach. This results from large longitudinal optical – transverse optical (LO-TO) splittings. We devised a first approximate scheme to include this and are planning to further explore it in future years. At the same time it focused our attention to this problem which appears to affect more systems than previously anticipated. 3) We continued our study of halide perovskites with an in-depth study of phonons and their relation to phase transitions. We also discovered that strong LO-plasmon coupling may be expected in these materials due to the low phonon frequencies and high plasmon frequency even for low carrier concentration due to the low electronic screening and extremely low hole mass.

Structure and Dynamics of Material Surfaces, interphase-interfaces and Finite Aggregates

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Funding: \$210,000 (2014)

PROGRAM SCOPE

This research program focuses on development, implementation and employment of quantum and classical simulation methodologies of predictive power, enabling their use as tools of discovery in investigations of the microscopic processes underlying generation and properties of novel materials in various forms and degrees of aggregation, under equilibrium and non-equilibrium conditions or subject to extreme environments. The program targets the elucidation of patterns in the size-dependence of materials properties where “small is different”, bridging the molecular, cluster and condensed-phase regimes. Topics in our research program include: 1. Nanoscale systems exhibiting unique structures, organizations, stabilities, reactivities, dynamics, and response patterns which endow them with unique physical and chemical properties. These systems include: (i) Gas-phase and surface-supported nanoclusters exhibiting structural isomerization transitions that gate their mobility and dynamic structural fluxionality, thus enabling their nanocatalytic activity. This includes studies of nano-catalyzed water splitting and generation of synthetic fuels. (ii) Nanocrystallites with superatom electron-shell structure stabilities, self-assembled into ordered superlattices, and exhibiting collective response mechanisms and unique optical and transport characteristics. 2. Bottom-up growth mechanisms of atomically precise graphene nanostructures. Investigations (using electronic structure, transport, and relativistic quantum field theory models) of topological effects in graphene nanostructures, including

graphene-based topological insulators and transport in atomically-precise segmented graphene nanoribbons. 3. The properties of confined electron and atom trapped systems exhibiting highly correlated, and entangled and spontaneous symmetry breaking; systems include semiconducting interfaces and graphene quantum nanostructures with and without external fields.

FY 2014 HIGHLIGHTS

(1) Hydrogen-bonded nano-silver superlattice: Structure and mechanical chiral response. Noble metal nanoparticles have had a deep impact across a diverse range of fields, including catalysis, sensing photochemistry, optoelectronics, energy conversion, and medicine . We reported [Nature Materials 13, Pg. 807 (2014)] the single-crystal X-ray structure of a superlattice made in the high-yield synthesis of $\text{Na}_4\text{Ag}_{44}(\text{p-MBA})_{30}$ protected –silver nanoparticles [our article in Nature 501, Pg. 399 (2013)], and found with quantum simulations that its structure and cohesion derive from hydrogen bonds between bundled p-MBA (para-mercaptobenzoic acid) ligands. The superlattice's mechanical response to hydrostatic compression was found to be characterized by a molecular-solid-like bulk modulus $B_0=16.7$ GPa, exhibiting anomalous pressure softening ($B_0' < 0$) and a compression-induced transition to a soft-solid phase. Such a transition involves ligand flexure, which causes gear-like correlated chiral rotation of the nanoparticles, pivoting about the hydrogen bonds that serve as hinges. The emergent behaviour of the superlattice assembly exemplifies the melding of the seemingly contrasting paradigms of 'small is different' and 'more is different'. Graphene - transport and topological effects in graphene nanoribbons (GNRs). Fundamental issues pertaining to the very nature of carriers in GNRs of variable width and edge terminations - namely, the crossover from ultra-relativistic to non-relativistic quantum behavior -which are of basic science interest as well as relevant for future applications of graphene, were addressed with numerical simulations and relativistic quantum-field position-dependent-mass model, unveiling fundamental clues and topological effects via analysis of Fabry-Perot-like oscillations in the electric conductance of GNR junctions. The work allows an effective treatment of a broad range of transport regimes in GNRs, [see Nature-Scientific Reports, Jan. 20 (2015)].

Strongly Correlated Electronic Systems: Local Moments and Conduction Electrons

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Funding: \$160,000 (2014)

PROGRAM SCOPE

The project focuses on the search for emergent phenomena in solids due to the strong correlations between electrons. The idea is that while the physics is governed by a relatively simple Hamiltonian, at low energy and low temperature, novel particles and fields may arise. An example we focus on recently is the emergence of Majorana fermions in solid state systems such as the ends of superconducting wires. We plan to explore novel phenomena associated with these Majorana fermions and look for signatures which may help in their detection.

FY 2014 HIGHLIGHTS

We discuss the problem of quasi-particle poisoning in Majorana fermions. The presence of quasi-particles breaks the parity conservation which is essential to protect the identity of the Majorana fermions. For any future application such as quantum memory or computation, it is crucial to know what the relaxation time is due to quasi-particle poisoning. We propose an experiment to measure this poisoning time. The result is published in Physical Review B89, 140505 (2014). In a second work we pointed out that Majorana fermions can lead to novel phenomenon of 'equal spin Andreev reflection'. Unlike conventional Andreev reflection, the reflected hole carries the same spin as the electron hitting the barrier. For certain polarization, the reflection is 100%. This can leave to a way to generate a highly polarized spin current. The result is published in Physical Review Letters 112, 037001 (2014).

Anharmonic and Thermal Effects Associated with Jammed Solids

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PROGRAM SCOPE

At the jamming transition, there are diverging length scales that lead to qualitatively new physics. As a result, a rigid packing at the zero-temperature jamming transition represents an extreme limit of a solid in several ways. In a well-defined sense, such a marginally jammed solid is the epitome of disorder; it is disordered and has the lowest possible rigidity. Thus, it lies at the opposite pole from a zero-temperature crystal where order is perfect. Moreover, at the jamming transition, the response to shear is infinitely weaker than the solid's response to compression. This is similar to the response of a liquid and distinguishes the jammed solid from a perfect crystal, where the ratio of the shear to bulk modulus, G/B , is of order unity. Finally, at the jamming transition, the regime of linear response shrinks to zero so that the solid is completely anharmonic; any infinitesimal stress forces the solid into non-linear behavior. One of our major objectives is to understand the anharmonic behavior of jammed solids. These include understanding the nature of the anharmonic vibration modes, looking in particular for anharmonic echoes. We will also study the particle rearrangements that occur when such a system is sheared or compressed beyond its limit of stability. A second focus of this work is to investigate to what extent an ordinary solid be described as lying between the two extremes of perfect order and complete disorder; can it be coherently described by perturbations around each limit? A third area builds on our recent work on the sensitivity of jammed solids to boundary conditions. Here we will study surfaces of amorphous packings, which can behave very differently from the bulk. This leads to a final objective, which is to understand the complicated role that temperature plays near the jamming transition.

FY 2014 HIGHLIGHTS

(1) Existence of linear response regime in jammed solids. The harmonic approximation is the foundation of much of solid state physics. Calculations that invoke this simplifying assumption are said to be in the linear regime. While the harmonic approximation is not exact, the existence of a linear regime is essential to our understanding of ordered solids. In two recent papers, we examined the effect of

nonlinearities in jammed sphere packings. We proved that that packings at densities above the jamming transition have a linear regime in the thermodynamic limit despite an extensive number of altered contacts. Thus, we showed that the harmonic approximation is on footing as firm for disordered solids as for ordered solids. (2) Between order and disorder: mechanical extremes of a solid. On first being introduced to solid-state physics, we typically learn about ideal perfect crystals. We are taught to describe real solids, which must always have imperfections, in terms of perturbations about crystalline order. However, such an approach only takes us so far: a glass, another ubiquitous form of rigid matter, cannot be described in any meaningful sense as a crystal with defects. Is there an opposite extreme to a crystal, an idealized solid with ``complete disorder,' that can be used as an alternate starting point for understanding real materials? We have shown that the solid made of particles with finite-range interactions at the jamming transition constitutes such an extreme limit. We found that jamming physics is not restricted to amorphous systems but instead is relevant and even dominates the behavior of solids with surprisingly high order. Our findings place the perfect crystal and the jammed solid as extreme poles from which one can understand mechanical behavior. Thus, ordinary matter should be thought of as existing somewhere on the continuum between these two idealized limits.

Charge Carrier Holes Correlations and Non-Abelian Physics in Nanostructures, Quantum Hall Effect and Hybrid Superconductor/Semiconductor Structures

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PROGRAM SCOPE

The goal of the project is to advance theory of spectra, interactions and correlations of charge carrier holes in nanostructures, including the effects of magnetic field and strain. Earlier unknown single-particle spin-orbit couplings in quantum dots and rings and new effective many-body interactions and correlations will be elucidated and explored. These features are absent in electronic systems but are specific to holes and can have profound impact on non-Abelian physics. We study paired and parafermion Fractional Quantum Hall effect states in 2D hole liquid. We will show that non-equidistant low-lying quantization levels in magnetic field in 2D hole Quantum Hall systems offer remarkable opportunity to control the Landau Level mixing by tuning carrier density and magnetic field simultaneously. It is then feasible to tune, the effective three-body correlations crucial in non-Abelian states. By numerically simulating two dimensional holes (2DH) in 001 grown GaAs via exact diagonalization, we expect to find the optimal setting for the non-Abelian fractional quantum Hall states. Some of the effects we plan to explore can also arise, but have never been studied, in two-dimensional electronic systems. We will investigate these cases as a test bed for our work on holes. We study novel correlated Quantum Hall states in the vicinity of crossings in 2D holes energy spectrum. Investigation of hole charge density wave states in high Landau levels, and their competition with other quantum Hall states at the crossing points. We also investigate novel charge density wave phenomena, especially caused by strain in both electron and hole 2D systems. We conduct theoretical study of Majorana Fermion excitations in hole nanowires proximity coupled to wave superconductors. We will demonstrate that spectral features of the charge carrier holes in quantum wires, newly emerging in our project, have profound effect on feasibility of observing Majorana physics.

FY 2014 HIGHLIGHTS

Our accomplishments for 2014. (I) Theory of Magnetic field spectral crossings in Luttinger holes in quantum wells: We showed an analytical solution for 2D holes in a quantum well in a magnetic field. The most important feature is coupling of the motion along the growth axis and the in-plane cyclotron motion as a result of Luttinger spin-orbit interactions. Our main finding is crossing of levels of holes in a magnetic field. We explained experiments on cyclotron mass and g-factor of 2D holes. (II) Calculation of hole spectrum and Haldane pseudopotentials for holes in a spherical geometry: We found spectra of Luttinger holes on a spherical shell, developing the procedure analogous to that for electrons. We obtained single particle states, with the spectrum identical to that of holes on the plane, and hole-hole interactions by calculating Haldane pseudopotentials. (III) Calculation of the effects of Landau Level (LL) mixing at ground state crossing in hole spectra: We calculated N-body interaction potentials, renormalizing hole-hole interactions in the presence of mixing of hole states in a magnetic field. We showed that variation of magnetic field near level crossings serves as a knob that tunes such mixing and enhances the 3-body interactions. Our preliminary results indicate that filling factor $\frac{1}{2}$ Fractional quantum Hall effect (FQHE) of holes exhibits excitations with non-Abelian statistics. (IV) Study of phase diagram and edge states of the filling factor 5/2 FQHE state with LL mixing and finite well thickness in a disc configuration: We find that due to the neutralizing background and LL mixing, there is a phase transition from the anti-Pfaffian to the Pfaffian states. LL mixing overcomes the effects of edge reconstruction and leads to an increased charge $e/4$ quasihole size. Due to finite thickness, these properties are enhanced dramatically. Only the Pfaffian and anti-Pfaffian states continue to possess energy gaps, while gaps for compressible stripe states close.

Geometric Phases and Topological Effects in Graphene and Magnetic Systems

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

We performed theoretical studies on electronic and transport properties of a) graphene systems, b) magnetic systems, c) topological insulators and superconductors, and d) MoS₂ and other two-dimensional materials.

FY 2014 HIGHLIGHTS

We predicted that a large anomalous Hall effect occurs in an important class of antiferromagnetic metals, Mn₃Ir and related materials. This prediction has motivated experimental efforts by a number of groups around the world aimed at performing studies of single crystal materials. We completed important theoretical studies of the fractional quantum Hall effect in graphene and of the quantized anomalous Hall effect in graphene on an antiferromagnetic substrate. The fractional quantum Hall effect in graphene represents a new frontier because of an approximate four-fold flavor degeneracy. We completed important new work on spin pumping and spin-transfer torques in antiferromagnetic metals.

This is an area of research that is growing rapidly in the moment. The pioneering work on this topic, now nearly ten years old, was supported by an earlier funding period of this DOE grant.

Electronic and Piezoelectric Phenomena in Nanostructures

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PROGRAM SCOPE

The electronic properties of graphene-derived nanomaterials, topological insulators and topological semimetals will be studied. Our proposed work develops and applies new theoretical models for understanding the low energy electronic properties of these materials and can guide their integration into electronic, optoelectronic and electromechanical applications. Specifically, we will study the electronic physics of multilayer epitaxial graphenes and new approaches to the study of topological insulators and semimetals. This work focuses on the development and application of theoretical methods that identify the microscopic role of symmetry, broken symmetries, and externally applied fields in controlling the quantum electronic behavior of these systems.

FY 2014 HIGHLIGHTS

Topological Dirac Semimetals in Three Dimensions Saad Zaheer (Penn Graduate Student) and E.J. Mele: We discovered that the two dimensional pseudo-relativistic physics of graphene near its charge neutrality point can be realized in three dimensional materials. In prior theoretical work this has been anticipated at phase transitions from inversion symmetric topological to normal insulators but this scenario requires fine tuning the electronic system to a critical point. Instead, our work identifies particular space-groups that allow 3D Dirac points as robust symmetry protected degeneracies in the bulk. These singularities are distinct from three dimensional chiral Weyl points: the Dirac singularities can be understood as a merger of Weyl nodes in a lattice where their annihilation is prevented by a crystallographic symmetry. We developed the nontrivial symmetry criteria necessary to identify these groups and, as an example, present *ab initio* calculations of beta-cristobalite BiO₂ which exhibits three Dirac points at the Fermi level. We predict that beta-cristobalite BiO₂ is a metastable material, so it is a candidate 3D pseudo-relativistic analog to graphene. Further, we predict a Dirac point like Fermi surface in three dimensional materials in a distorted spinel structure. The predictions are based on density functional theory as well as phenomenological $k \cdot p$ symmetry analysis. The four examples identified are: BiZnSiO₄, BiCaSiO₄, BiMgSiO₄ and BiAlInO₄. These systems are electronically three dimensional analogs of graphene and will host rich low energy topological phenomena. Reference: S.M. Young, S. Zaheer, J.C.Y. Teo, C.L. Kane, E.J. Mele, and A.M. Rappe "Dirac Semimetal in Three Dimensions" Phys. Rev. Lett. 108, 140405 (2012); J. A. Steinberg, S.M. Young, S. Zaheer, C.L. Kane, E.J. Mele and A.M. Rappe "Bulk Dirac Points in Distorted Spinel" Phys. Rev. Lett. 112, 036403 (2014).

Theory of Surface and Interface Physics of Correlated Electron Materials

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PROGRAM SCOPE

The aim of this project is to develop and apply the theoretical tools necessary to understand the properties of surfaces and interfaces involving materials exhibiting strong electronic correlations (such as high transition temperature superconductors, colossal magnetoresistance manganites, and Mott metal-insulator systems), with the aims of (a) using the systems as a lens for understanding fundamental issues in correlated electron physics, (b) uncovering new physics existing at surfaces and interfaces, and (c) establishing modalities for controlling phenomena which may be useful in energy and device applications.

FY 2014 HIGHLIGHTS

We have provided new insights into the density functional plus dynamical mean field method widely used to study correlated materials, showing that standard theory wrongly predicts that many Mott insulators are metals and gives an incorrect estimate of the charge transfer across oxide interfaces, identifying the key issue of the energy splitting between oxygen and transition metal orbitals and introducing a new double counting method that corrects the problems. We also extended the density functional plus dynamical mean field theory methodology to enable the first total energy calculations including lattice relaxations with this method. This methodological advance will be important for future work because it enables the determination of structures of correlated electron materials. In collaboration with an experimental colleague, A. Pasupathy, and a former postdoc, R. Fernandes, we obtained results which challenge one of the basic tenets of metal physics. Our theoretical calculations, combined with Pasupathy's scanning tunneling microscopy measurements of the surface of NaFeAs (parent compound of the iron-pnictide family of high T_c superconductors) showed that the apparently conventional fermi liquid phase of the material is in fact characterized by very large amplitude, very slowly fluctuating wave of spin density order, made visible by the scattering off of impurities, far beyond the linear response picture believed to describe fermi liquid metals.

Optical, Transport Phenomena, and Interaction Effects

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PROGRAM SCOPE

We study physics of chiral electron states, whose properties depend on the direction of electron propagation. Such states exist in a variety of practical realizations: two-dimensional electron gas in semiconductor quantum wells with spin-orbit interaction, Dirac fermions in graphene (2D) or carbon nanotubes (quasi-1D), protected surface states in topological insulators, etc. The emphasis is on investigating transport phenomena and effects of electron-electron interactions from a general perspective, on elucidating features common to various chiral systems, and on applying to newer materials the techniques previously proved successful for other chiral systems. As an example, the method of transport equations used by us to study spin Hall effect was subsequently applied to the problem of optical conductivity in graphene, within the scope of this project. Among specific problems currently studied are properties of collective plasmon modes in graphene, effects of resonant impurities on properties of graphene and topological insulators, the role of many-body effects on the optical properties of carbon nanotubes. We employ broad range of methods including quantum transport theory based on kinetic equations, diagrammatic technique, hydrodynamics of electron liquid, etc. Both analytical as well as numerical approaches are utilized. As far as the fundamental physics is concerned, our main effort is to study transport phenomena and effects of electron-electron interactions from a general perspective of elucidating features common to various chiral systems.

FY 2014 HIGHLIGHTS

We have developed a quantum-mechanical approach to calculating equilibrium particle currents along the edges of systems with nontrivial band spectrum topology. Our approach does not require any a priori knowledge of the band topology and, as a matter of fact, treats topological and nontopological contributions to the edge currents on the same footing. To illustrate the application of our method we demonstrated the existence of “topologically nontrivial” particle currents along the edges of three different physical systems: two-dimensional electron gas with spin-orbit coupling and Zeeman magnetic field, surface state of a topological insulator, and kagomé antiferromagnet with Dzyaloshinskii-Moriya interaction.

Simple Metals at High Pressures and Impact of Spin-Orbit in 5d Atom Compounds by Electronic Structure Quantum Monte Carlo Methods

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PROGRAM SCOPE

Our research is focused on development and application of advanced many-body methods to calculations of spin, electronic and atomic structures and optical properties of energy-related materials. We employ correlated wave function approaches such as electronic structure quantum Monte Carlo (QMC) which is capable of overcoming the limitations of traditional methods in explicit treatment of electron many-body phenomena. This promising methodology enables us to study problems which are at the forefront of condensed matter physics such as materials with strong correlations and complex

systems with competitions of many-body effects. Our QMC investigations are focused on several application and method development areas. In particular, we plan to study alkali and alkaline metals at high pressures such as Li, Na, Be and others, with the goal of evaluating energy differences between competing or nearly degenerate structures and establish thus high accuracy QMC data for these systems. We plan to develop the QMC methodology for more accurate description of both metallic and insulating solid phases. For 5d and heavier elements the spin-orbit interaction (SOI) becomes very important and we plan to develop QMC methods with explicit treatment of spins as quantum variables and study such SOI effects in this class of materials. These developments will be based on our recent calculations of spin-orbit interactions in atoms using variational Monte Carlo method with the goal to generalize the QMC methodology to the more accurate QMC projector approaches.

FY 2014 HIGHLIGHTS

The project was initiated in September 2014 and the postdoctoral research associate was hired from October 1st. We have started preparations for quantum Monte Carlo (QMC) runs of Li systems based on our previously carried out preliminary calculations. In collaboration with A. Ambrosetti and F. Pederiva (U. Padova, U. Trento, Italy) we have been involved in development of QMC methods for spin-orbit interactions and one of the testing systems has been a fermi gas with repulsive interactions and Rashba spin-orbit coupling. This has led to new calculations that enabled to study, for example, the onset of Stoner instability and also validation of the developed methodology for studies of competing spin-orbit and correlation effects in periodic systems.

Nonequilibrium Phenomena in Topological Insulators

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PROGRAM SCOPE

The aim of the project is to study two-dimensional and three-dimensional topological insulators under out of equilibrium conditions such as an applied bias voltage and external irradiation by light. The goal is to explore what kinds of topological phases of matter can be stabilized under the combined effect of drive and dissipation. Specific systems that will be studied are Floquet topological insulators where a laser can modify topological properties. The project will also explore the effect of interactions and dissipation on driven topological insulators, and on hybrid topological insulator-ferromagnetic systems.

FY 2014 HIGHLIGHTS

Graphene irradiated by a circularly polarized laser has been predicted to be a Floquet topological insulator (TI) showing a laser-induced quantum Hall effect. A circularly polarized laser also drives the system out of equilibrium resulting in non-thermal electron distribution functions that strongly affect measurable quantities. The PI's group has made significant progress in understanding Floquet TIs by fully accounting for the inherently non-equilibrium nature of these systems, and by also accounting for dissipative mechanisms. Theoretical predictions for experimentally measurable quantities such as

photo-emission spectra as well as the Hall conductance have been obtained. While for a closed system with no external dissipation, the Hall conductance was found to be far from the quantized limit due to the system retaining memory of its initial state, coupling to a sufficiently low temperature reservoir of phonons was found to produce effective cooling, and thus an approach to the quantum limit, provided the frequency of the laser was large as compared to the band-width. For laser frequencies comparable to the band-width, strong deviations from the quantum limit of conductance was found even for a very low temperature reservoir, with the precise value of the Hall conductance determined by a competition between reservoir induced cooling and the excitation of photo-carriers by the laser. The results for the open system were obtained by solving a Floquet kinetic equation that accounts for phonon-induced inelastic scattering between different quasi-energy levels.

Modeling the Self-Assembly of Ordered Nanoporous Materials

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PROGRAM SCOPE

This project is about modeling the assembly processes in the synthesis of nanoporous materials. Such materials are of enormous importance in modern technology with application in the chemical process industries, biomedicine and biotechnology as well as microelectronics. An ongoing theme in porous materials science and engineering is the tailoring of pore structure for specific applications. Silicate and aluminosilicate chemistry provides an enormously valuable route to stable nanoporous materials. The number of possible materials structures is almost without limit. The origin of this is the low coordinate bonding in these materials and the uniformity of binding energies between different structures. We focus on two classes of materials: microporous crystalline materials, such as zeolites, and ordered mesoporous materials. In the first case the pores are part of the crystalline structure, while in the second the structures are amorphous on the atomistic length scale but have order on the length scale of 2 - 20 nm. Our models are based on the assembly of corner sharing silica tetrahedra in the presence of structure directing agents. Our modeling approach is the first to capture silica polymerization, nanopore crystallization, and mesopore formation through computer-simulated self assembly. We are applying both lattice and off-lattice models to shed new light on zeolite nucleation. The first component of this is the study of silica polymerization across a broad pH range. We then consider the nucleation of all-silica zeolite analogs modeled using transition path sampling applied to our lattice model of silica. The final component involves the study of pathways connecting amorphous and ordered phases. For ordered mesoporous materials we are investigating issues like the influence of surfactant chain length on the cooperative templating of mesoporous structures, as well as the interplay between silica polymerization and mesoscale surfactant assembly.

FY 2014 HIGHLIGHTS

(1) Off-Lattice Modeling: We have developed a reactive parallel tempering Monte Carlo method for searching for ground state structures of our off-lattice model of silica polymerization. This method generalizes parallel tempering to the case where the tempering variable is the equilibrium constant for

the silica condensation reaction. This Monte Carlo simulation approach can form a variety of phases of silica including both dense silica polymorphs and some zeolite frameworks. We are extending our work on mesoporous silica synthesis to our off-lattice model of silica polymerization. This has involved a new coarse-grained model for water-surfactant-silica systems and a new Monte Carlo / molecular dynamics method for simulating both mesophase formation and silica polymerization. (2) Lattice Model: We have extended our lattice model of silica polymerization over a broad pH range, by modeling the addition of organic structure directing agents alongside hydroxide to tune pH. Our simulations have revealed the transition from gel formation at low pH and high silica concentration, to the nanoparticle regime at high pH and low silica concentration. This work has appeared in the following article: M. N. Khan, S. M. Auerbach, and P. A. Monson, "Lattice Model for Silica Polymerization: Monte Carlo Simulations of the Transition between Gel and Nanoparticle Phases," J. Phys. Chem. B 118, 10989-10999 (2014). We have introduced templates into our parallel tempering simulations for finding ground states of the lattice model of silica. This has led to the formation of new structures that were not formed in the absence of the template, and has generated new insights into the impact of template size and concentration on the structures produced. Review Article: We published an invited review article based upon our DOE-funded work, "Modeling the Assembly of Nanoporous Silica Materials", S. M. Auerbach, W. Fan, and P. A. Monson, International Reviews in Physical Chemistry, 34, 35-70 (2015).

Non-Equilibrium Physics at the Nanoscale

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Funding: \$330,000 (2014-2016)

PROGRAM SCOPE

Experimental advances in the fabrication of nanoscale systems have provided us with the unprecedented opportunity to investigate non-equilibrium transport phenomena from the atomic to the mesoscale in a wide variety of materials. The ability to visualize the flow of charge or energy at smaller and smaller length scales allows us to establish a fundamental connection between the transport properties of nanoscopic systems at the atomic and global scale, enabling the development of smart and functional nanoscopic components for energy research and quantum computation. The objective of this research program is to develop a comprehensive theoretical framework to investigate complex non-equilibrium transport phenomena in nanoscopic systems. This program will (a) identify the key elements that govern non-equilibrium charge and energy transport in nanoscopic systems, such as interactions, geometry, or topology, (b) determine how these elements shape the relation between local and global transport properties, and (c) identify the basic principles required for the quantum design of transport properties. To achieve these objectives, this program will employ field-theoretical non-equilibrium methods to investigate how the emergence of complex correlations, driven by the interplay between interactions, electronic symmetries, disorder and the coupling to external environments, determines the non-equilibrium transport properties in nanoscopic realizations of correlated Kondo systems, topological insulators, graphene, and photovoltaic materials. These projects will establish a constructionist framework to describe, control, and quantum design charge and energy transport at the nanoscale by identifying the signatures of strong correlations in non-equilibrium transport, by demonstrating how the flow of charge and spin can be manipulated at the atomic scale through lensing, strain and the creation

of topologically non-trivial states, and by establishing criteria for optimal energy transport in photovoltaic materials.

FY 2014 HIGHLIGHTS

Rapid advances in quantum computation and spin electronics, heralded by the discovery of topological insulators, have been hampered by the inability to control the flow of spin and charge at the nanoscale. We demonstrated that such control can be established in nanoscopic two-dimensional topological insulators by breaking their time reversal symmetry via magnetic defects. This allows for the emergence of two novel phenomena: the creation of nearly 100% spin-polarized charge currents, and the design of highly tunable spin diodes. These phenomena are robust against edge disorder and dephasing effects, and thus provide a new venue for controlling the flow of spin and charge. We developed a non-equilibrium Keldysh Greens function formalism to study excitonic energy transport in hybrid organic-inorganic perovskites and biological complexes. We succeeded in identifying the relation between global and local transport properties in light-harvesting biological complexes, such as the total exciton flux, the spatial exciton flow pattern, the local recombination rate, and the local exciton density. This approach is ideally suited to elucidate the microscopic model underlying efficient energy transport and to reveal the conditions necessary to optimize it. We proposed a novel theoretical approach to identify the microscopic mechanism of heavy fermion Cooper pairing. By elucidating the relation between non-equilibrium transport and electronic structure, we extracted the momentum form of the magnetic interactions between f-electron moments in CeCoIn₅ from experimental quasi-particle interference (QPI) spectroscopy. This allowed us to make a series of quantitative predictions for the symmetry and magnitude of the superconducting gap, the critical temperature, and phase-sensitive QPI spectra. Their good quantitative agreement with experiments provides strong evidence for f-electron mediated Cooper pairing as the origin of heavy-fermion superconductivity.

Spin-Orbit Tailoring of Materials Properties

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PROGRAM SCOPE

Spin-orbit coupling (SOC) rose in visibility almost a decade ago with the discovery of topological insulators (TIs) based on SOC and inverted bands. SOC connects the direction of the electron's orbital moment with that of its spin moment, while having an effect on both and coupling to magnetic order and to the lattice. For TIs the impact is qualitative – a matter of fact rather than one of magnitude, and small couplings may still be important. For most other areas of application of SOC (and for TIs as well) the magnitude is important. In this project we extend our earlier computational discoveries of surprisingly large orbital moments in 3d oxides up to 0.7 Bohr magnetons, an order of magnitude larger than had been obtained for 3d systems. 4d and 5d materials, with much larger SOC, are being studied. For both 3d and 5d oxides the interplay between SOC and strong correlation provides a rich platform for several types of behavior, and symmetry breaking is found to be a crucial factor in determining the ground and low energy excited states.

FY 2014 HIGHLIGHTS

The interplay and competition between several comparable energy scales has been studied in several systems. The energy scales are spin-orbit coupling strength, repulsive Coulomb interaction, Hund's exchange energy, crystal field splitting, and bandwidth. For open shell cations in oxides, breaking of symmetry is the dominant feature, and enlarged simulation cells must be adopted to allow the many underlying symmetries to be violated by the interactions. $\text{LaNiO}_3/\text{LaAlO}_3$ multilayers provide a vivid example, displaying a combination of charge, spin, and orbital order with also a lowering of structural symmetry. In the heptavalent Os^{7+} compound KOsO_4 , symmetry breaking by structure and by spin-orbit coupling enables an orbital moment to emerge in the e_g subshell, something that is impossible in cubic symmetry. Our theoretical study of a newly synthesized quadruple perovskite (a former student is a member of the synthesis team) $\text{CaCO}_3\text{V}_4\text{O}_{12}$ is showing it to be one of the most intricate systems yet studied by (correlated) density functional theory, with charge states (and associated moments, orbital occupations, and structural distortions) of both Co and V feeding back on each other. Lastly, the mixed valent niobate $\text{Nb}_{12}\text{O}_{29}$ has been found to be a novel and highly anisotropic Heisenberg-Kondo lattice system.

Complex (anti)ferroic Oxides: Statics and Dynamics at Finite Temperatures

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PROGRAM SCOPE

Complex oxides that exhibit ferroic, antiferroic or multiferroic properties are of extreme fundamental and technological importance. Fundamentally such materials are very attractive because they exhibit delicate energy competitions which result in the appearance of some spontaneous property (magnetization, electric polarization or strain) or particular type of ordering. Technologically they are in the heart of numerous applications. A few examples include memory applications, pyroelectric sensors, pressure sensors, capacitors, optical communications, ultrasonic motors, phase-array radars, ultrasound imaging and actuators, thermistors, filters, light detectors, high-power microwave devices, and many others. However, despite their special role in both fundamental and applied sciences, many such materials and their properties remain rather poorly understood. Some examples include statics and dynamics of antiferroelectrics and relaxors, exotic energy conversion mechanisms in (anti)ferroics, fundamental intrinsic dynamics of such materials, and (anti)ferroic phenomena at the nanoscale. Such lack of understanding critically hinders both scientific and technological progress, especially as it applies to the nanoscale. The ultimate goal of this project is to achieve a fundamental understanding of statics and dynamics of complex oxides that exhibit ferroic, antiferroic, multiferroic or relaxor properties at both macro- and nano-scales through state-of-the-art computer simulations. The potential outcomes of this research include (1) state-of-the-art computational tools for modeling static and dynamical properties of bulk and nanoscale complex (anti)ferroic oxides; (2) deep atomistic understanding of energy converting mechanisms in such materials; (3) fundamental understanding of dynamical properties of (anti)ferroics and relaxors at microwave and infrared frequencies.

FY 2014 HIGHLIGHTS

1. We have achieved a systematic understanding of the role of mechanical boundary conditions in the soft mode dynamics (J. Phys.: Condens. Matter 26, 435901 (2014)). 2. We have established the possibility to drastically alter electric response of ferroelectric ultra-thin films by partial charge compensation. (Appl. Phys. Lett. 104, 012909 (2014)). 3. We have developed a force-field to study finite-temperature properties of antiferroelectric PbZrO_3

Theoretical and Computational Studies of Characteristics of Metallic Nanostructures

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PROGRAM SCOPE

Our work focuses on understanding structure-function relationship in nanomaterials so as to enable the long term goal of rational design of functional materials, which are of immense scientific and technological interest. We are particularly interested in understanding factors that control the magnetic and optical properties of these materials and their response to ultrafast external fields. Part of our effort is in developing and applying appropriate theoretical and computational techniques which provide more accurate descriptions of excited and bound states, and electron correlation effects than afforded by the popularly used density functional theory (DFT). To ensure dynamical stability of nanostructures we also determine their vibrational dynamics and thermodynamics. Additionally, we develop non-adiabatic techniques to expose the non-equilibrium behavior of nanosystems, as in the presence of external fields. Through systematic study of characteristics for a set of selected materials and corroboration of their results with experimental data, we formulate rules and guidelines for predictive material design. The research stages in the different projects include determination of one or more of the following: 1) the geometric and electronic structure of lowest energy structures using reliable schemes (e.g. DFT); 2) vibrational dynamics and thermodynamics through density functional perturbation theory (DFPT); 3) magnetic properties via our nano-DFT+ DMFT (dynamical mean field theory) approach; 4) optical response, using time dependent density functional theory (TDDFT) and its density matrix version as proposed by us for systems with bound states, multiple excitation and strong correlation effects; 5) development of the non-adiabatic time dependent spin density function theory NA-TD-SDFT; 6) structural evolution of nano-sized systems using self-learning kinetic Monte Carlo (SLKMC) simulations.

FY 2014 HIGHLIGHTS

(1) Non-adiabatic Time-Dependent Spin-Density Functional Theory for strongly correlated systems: With our proposed methodology for calculating a frequency dependent exchange-correlation functional we can describe spectral properties of strongly-correlated systems such as YTiO_3 within multi-orbital time-dependent spin-density functional theory. Calculation of the nonequilibrium response of YTiO_3 under an applied short laser pulse shows novel behavior of its charge dynamics. Our DFT + Nonhomogeneous DMFT approach for finite systems when applied to determine the magnetic properties of Fe nanoparticles containing up to 147 atoms, displays much better agreement with the experimentally

observed non-monotonous dependence of magnetization as function of cluster size than that obtained from the DFT and DFT+U approaches. (2) Magnetocrystalline anisotropy (MCA) of FePt nanoparticles: We find an enhancement of MCA for the FePt nanoparticles containing up to 150 atoms as compared to that of Fe nanoparticles of the same size and geometry and bulk FePt with L_{10} structure. We trace this enhancement to the increased spin and orbital moment of Pt atoms which raises the spin-orbit coupling constant. Our DFT study of geometric, electronic, and magnetic properties of $\text{Fe}_x\text{Au}_{113-x}$ ($x=23, 56, 90$) nanoparticles shows preference for the core-shell structure with the Fe core maintaining magnetic moment of $\sim 2.8 \mu_B$, which is 27% enhancement from the bulk value, and correlated with the local coordination of Fe atoms and with the charge depletion from Fe to Au atoms. (3) Tuning plasmon excitations in transition-metal doped arrays of noble-metal nanochains: For pure noble and transition metal (TM) chains we find that as the number of chains in the array increases the plasmon peak shifts to higher energies and appears in the visible range for an array of three gold chains, each consisting of more than 10 atoms.

Theoretical Investigations of Single Particle Spectroscopies of Novel Materials

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PROGRAM SCOPE

The goal of this project is to gain insight into the properties of novel quantum materials using theoretical and computational modeling of electron correlations. We have focused on several problems in this general area. First, we have investigated magnetism in correlated oxides and oxide interfaces, using both microscopic modeling of exchange and anisotropy in the presence of spin-orbit coupling and continuum field theory descriptions of effective interactions. This has led to new insights into stabilizing topological spin textures known as skyrmions in low dimensional chiral magnets. Second, we have continued our work on high T_c superconducting cuprates in the underdoped region. Our goal is to understand the interplay between the normal state pseudogap seen in spectroscopies and additional order parameters, like charge density waves (CDW) which compete with superconductivity, and lead to the Fermi surface reconstruction observed in quantum oscillations. As part of this effort, we have developed the formalism to describe quantum oscillations in a vortex liquid state, which has short range pairing correlations in addition to a density wave that breaks translational symmetry. Finally, we continue to collaborate with the experimental group at Argonne National Labs on analysis of angle resolved photoemission spectroscopy and x-ray data on superconducting and CDW materials.

FY 2014 HIGHLIGHTS

(1) Most theoretical studies of skyrmions have focused on chiral magnets with broken bulk inversion symmetry, where the skyrmion crystal phase is stabilized in a rather small regime of parameter space by easy-axis anisotropy. In contrast, we considered 2D and quasi-2D systems with broken surface inversion [PRX 4, 031045 (2014)] and showed that skyrmion crystals are more stable over a much broader range of parameters than in 3D. We pointed out the importance of easy-plane anisotropy, and show that it arises naturally from the same spin-orbit coupling that leads to the chiral Dzyaloshinskii-Moriya (DM)

interaction. These results are directly relevant for magnetic thin films and for magnetism at oxide interfaces. (2) We demonstrate in a simple model the surprising result that turning on an on-site Coulomb interaction in a doped band insulator leads to the formation of a half-metallic state. Our results [PRL 112, 106406 (2014)] suggest a new route to half metallic behavior, and will hopefully motivate searches for new materials for spintronics. (3) We have developed a theoretical framework for describing quantum oscillations in a phase fluctuating superconductor where the pairing correlations are short ranged in both space and time. Building on our 2013 Nature Communication paper on this topic, we have been systematically comparing the results of a semi-classical analysis with that of a more rigorous analysis in the Landau level basis. (4) We have collaborated with the Argonne group on the analysis of photoemission, x-ray and scanning tunneling microscopy data on the CDW material 2H-NbSe₂ intercalated with Mn and Co. We find that both at high temperatures and at large intercalation, the CDW order becomes short-ranged due to fluctuations of its phase, while a well-defined amplitude persists and gives rise to an energy gap in the electronic excitation spectrum.

First-principles Investigations of Fundamental Physics and New Materials for Optoelectronic Applications

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PROGRAM SCOPE

By using first-principles electronic structure methods, we investigate the fundamental physics of optoelectronics and design materials with the specific optoelectronic properties. These studies require understanding of electronic structure, including modeling light absorption, photovoltaics, and photoconductivity. The solar cell, one of the most important applications of optoelectronics, has attracted a great deal of attention due to the demand for new energy sources. However, the power conversion efficiency of solar cells based on p-n junction is subject to the Shockley-Queisser limit. The bulk photovoltaic effect (BPVE) in materials without inversion symmetry has been proposed as an efficient way to transform solar energy. In particular, ferroelectric materials with spontaneous polarization can separate light-induced carriers. Therefore, finding ferroelectric materials with band gaps in the visible light range, strong polarization, and high BPVE is a promising direction for solar cell research and toward other optoelectronic applications. We computationally design materials with low band gap and high polarization. Several strategies have been proposed: solid solutions with partially substituted A or B-site cations in perovskites, defects, and structural transition induced band gap reduction. Once we have materials with a proper band gap, we explore whether they can show strong BPVE. In the meantime, we investigate the effects of strain, stress, electronic correlation, and phonons on the BPVE of the material, particularly, ferroelectrics. We perform materials design to find materials with high BPVE. Based on our understanding of optoelectronics and our material design strategies, we can build connections between the material composition and structural phase, and the material light response. Therefore, our project can guide the development of new materials for solar cell applications and other areas related to light-matter interaction in solids.

FY 2014 HIGHLIGHTS

By using first-principles methods, we have computationally designed a series of Zn^{2+} partially substituted KNbO_3 perovskite solid solutions, showing lowered band gaps within the visible light range. More generally, we propose a strategy to substantially reduce the band gap by as much as 1.2 eV, while maintaining relatively high polarization through local rhombohedral-to-tetragonal structural transition in perovskites. Hybrid halide perovskites can show as much as 20% power conversion efficiency. These materials are showing great potential as next generation solar cell materials. We have demonstrated that BPVE plays an important role in providing such high efficiency. This can potentially explain the observed large open-circuit voltage and I/V hysteresis in hybrid halide perovskites. Besides perovskites, other types of materials were also extensively investigated for optoelectronic applications. LiAsSe_2 , LiAs_2 and NaAsSe_2 can show large BPVE, and their optical dielectric constant displays substantial enhancement induced by stress. With low band gaps and high optical responses, these materials have potential for use as bulk photovoltaics.

Next Generation Photon and Electron Spectroscopy Theory

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PROGRAM SCOPE

Our research program aims to develop quantitative theories and associated codes for next-generation calculations of photon and electron spectroscopies. A main goal is to incorporate correlation effects beyond the quasi-particle approximation over a spectral range from the visible to x-ray energies. Our approach is based on first principles methods, e.g., real-space multiple-scattering and Bethe-Salpeter equation (BSE) techniques, which are implemented in the FEFF and OCEAN codes developed in our research program. These many-body effects include inelastic losses, core-hole interactions, vibrations, and now strong correlations, effects for which accurate theories are among the most challenging problems in condensed matter theory. Practical theoretical developments are essential to obtain predictive calculations of optical and x-ray spectra and other excited state properties for a wide class of materials. Consequently our research is important for advancing fundamental theoretical understanding of materials properties. Indeed, our codes are in use world-wide for interpreting x-ray spectra, e.g., at DOE synchrotron x-ray facilities, as documented by thousands of citations. Besides x-ray absorption, x-ray emission, and x-ray photoemission spectra, our computational methods are applicable to new spectroscopies including RIXS (resonant-inelastic x-ray scattering), and spectra from time-dependent x-ray sources.

FY 2014 HIGHLIGHTS

A major highlight of our recent research has been the development of an approach for treating many-body effects in x-ray and electron-spectroscopies based on cumulant-expansion methods. Rather than wave-functions, this powerful theoretical formalism is based on an exponential form of the electron Green's function in the time-domain, and naturally builds in effects beyond the quasi-particle

approximation, including vertex corrections. The method has proved to be advantageous compared to conventional GW approaches, yet simplifies the calculations. This effort was a major topic of our research project and is leading to a number of breakthroughs. A recent success is the treatment of multiple plasmon satellites in the XPS spectra of materials ranging from graphite to graphene. Another is an improved calculation of spectral functions and electron correlation energies. Remarkably we recently found that the cumulant method can be applicable to strongly correlated systems. For example, we showed that a real-time calculation of the cumulant explains the charge transfer satellites in x-ray photoemission spectra. These satellites characterize strong local correlations which have been formidably difficult to treat with first principles, e.g., configuration-interaction, methods. Notable improvements have also been made to our spectroscopy codes: our GW/Bethe-Salpeter Equation code OCEAN has been extended to treat large systems such as water and ice, and our real-space Green's function code FEFF has been extended to include Hubbard-model corrections in f-electron systems. Finally in collaboration with the Northeastern University group, we have developed a novel way to calculate many-body edge singularity effects in RIXS.

Strongly Correlated Electron Systems

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PROGRAM SCOPE

The program's scope is the theoretical investigations of the many-body effects and the ensuing collective modes that are manifested by actinide materials. One focus of the program is the enigmatic phase transition exhibited by URu_2Si_2 at low temperatures, which has evaded classification for over 25 years. The possibility that the transition is characterized by an order parameter which is of an entangled spin and orbital is studied. Such an entangled order parameter is not measurable through standard experimental probes, which may explain why this phase transition remains enigmatic. Properties, such as the phase diagram under pressure and magnetic field, are studied theoretically. The collective modes related to the ordering are also being investigated. A second focus is the unusual magnetic anisotropy found in the collective magnetic excitation spectra of the cubic uranium mono-chalcogenides. The research focuses on the effects of the Hund's rule exchange and the spin-orbit coupling. The research utilizes a description based on the under-screened Anderson lattice Model. A third focus is the collective modes that have been observed in some paramagnetic heavy-fermion semiconductors and semimetals. This includes SmB_6 which has been recently re-classified as a Topological Kondo Insulator. The relation of the magnetic modes to critical fluctuations is being studied together with the effect of doping that may induce a Lifshitz transition. The scope of the project also includes studies of Intrinsically Localized Modes, or persistent lattice vibrations with finite spatial extents. Unusual anharmonic lattice vibrations, which are not described by the usual harmonic theory of phonons, have been reported in alpha-uranium at high temperatures. The possibility of Intrinsically Localized vibrational Modes (ILMs) occurring in plutonium compounds are being investigated in this program.

FY 2014 HIGHLIGHTS

The Fermi surface of URu_2Si_2 has been studied experimentally and theoretically. It has been found that the Fermi-surface reconstructs at the transition, and results in a doubling of the size of the unit cell. The experimental results are consistent with a change of the electronic symmetry from body-centered tetragonal to simple tetragonal, without there being any change in the atomic positions. Therefore, the transition has been identified as involving a nesting of the Fermi-surface through the $(1,0,0)$ reciprocal lattice vectors. The folding of the electronic Brillouin zone has been identified as producing a gap on most of URu_2Si_2 's Fermi surface. ILMs have been extensively studied in idealized one-dimensional classical systems. We have investigated the occurrence of ILMs one-dimensional quantum systems, and have shown that this can be generalized to three-dimensional systems. In one-dimension, we found that ILMs are produced by anharmonic interactions and occur even for the smallest interaction strength due to divergences in the one-dimensional two-phonon density of states. This work has been shown to be generalizable to higher dimensions. However, the ILMs only occur for specific center of mass momenta. The special volumes of momenta occur on high symmetry lines that are close to the Brillouin zone boundary. The reason for ILMs to occur only in these special regions of the Brillouin zone, is that the van-Hove singularities in the two-phonon density of states coalesce and become large and perhaps even divergent. The large value of the density of states at the edges of the two-phonon continuum enables the anharmonicity to produce ILMs at energies outside the continuum. This work also includes a group theoretic analysis which shows that the spectrum of ILMs have internal quantum numbers and intrinsic spins of either $S=0$ or $S=2$. The $S=2$ bosonic excitation would come close to providing a solid state version of the graviton.

Fundamental Studies of Complex Oxides and Their Interfaces

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PROGRAM SCOPE

This project is devoted to a theoretical study of the physics of the complex oxide materials and their interfaces. These materials come with complex crystal structures, with metal-oxygen octahedra, bringing in the electron-lattice coupling via the Jahn-Teller effect, competing magnetic interactions such as double exchange and super exchange, and spin-orbital coupling. In addition, strain and polar interfacial potential could drastically alter the bulk behavior, resulting in an interface, with behavior drastically different from either of the parent materials. An example of this is the formation of a two dimensional electron gas at the $\text{LaAlO}_3/\text{SrTiO}_3$ polar interface and the rich variety of phases observed there. The objective of this proposal is: (1) To develop a microscopic understanding of the observed behavior in the complex oxides and their interfaces and (2) To develop key concepts of interface physics incorporating the insight gained from the density-functional calculations. The intellectual challenge is to understand the strong interplay between a variety of effects such as the strong correlation, Jahn-Teller effect, orbital ordering, coupling between the spin, charge, and orbital degrees of freedom, competing magnetic interactions, etc., which results in a rich variety of phenomena in these materials. We have carefully selected a few specific problems for study based on potential new physics and current

experimental efforts. The proposed research topics include closely related problems in the correlated oxide physics, viz., (i) Rashba spin-orbit effect at the oxide surfaces and interfaces, (ii) Possible origin of the Kosterlitz-Thouless transition at the $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces, (iii) Spin-Orbital ordering in the frustrated spin-ice oxides, and (iv) Development and Incorporation of the Gutzwiller density-functional approach into the muffin-tin orbitals method for correlated systems. Close interaction with the experimenters is envisaged.

FY 2014 HIGHLIGHTS

1) Rashba Effect in the Oxide Surfaces and Interfaces -- One highlight of our research was a study of the Rashba effect in the oxides. The effect describes the momentum-dependent spin splitting of the electron states and is the combined result of the spin-orbit interaction and the inversion-symmetry breaking. The effect is at the heart of a class of proposed spintronics devices. In this work, we showed that the Rashba effect in the perovskite structures can be tuned by manipulating the two-dimensional electron gas (2DEG) by an applied electric field, using it to draw the 2DEG in or out of the surface. These ideas were studied by a comprehensive density-functional study of the recently discovered KTaO_3 surface. Analytical results obtained with a tight-binding model unraveled the interplay between the various factors affecting the Rashba effect. 2) Electronic structure of $\text{Ba}_3\text{CuSb}_2\text{O}_9$: A candidate quantum spin liquid compound -- Using density functional methods, we studied the electronic structure of the title quantum spin liquid compound. While Cu atoms are expected to be Jahn-Teller centers, no distortions are observed in the system suggesting a dynamical Jahn-Teller effect and the issue was under intense debate. Solving a simple model by exact diagonalization, we showed that the electronic correlation effects in general enhance the tendency towards a Jahn-Teller distortion by reducing the kinetic energy due to correlation effects. Our calculations did indeed show a significant Jahn-Teller distortion, when we included the correlation effects within the Coulomb-corrected GGA + U method. We argued for the presence of a random static Jahn-Teller distortion rather than a dynamical effect because of the potential fluctuations inherently present in the system caused by a significant disorder. This work helped clarify the nature of the electronic structure and especially of the Jahn-Teller effect in this material.

Strongly Correlated Electrons

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PROGRAM SCOPE

Strongly correlated electron systems continue to be a central problem in condensed matter physics. Many phenomena are still awaiting an explanation and new effects of potential technological relevance are being discovered. The purpose of the study is to gain further insight into the mechanisms and properties of correlated electron systems. This proposal addresses aspects of heavy fermions, such as quantum criticality due to antiferromagnetic correlations, the temperature and field dependence of the NMR relaxation in the topological Kondo insulator SmB_6 , quantum criticality in ferromagnetic Kondo systems such as YbNi_4P_2 , and the hidden order phase in URu_2Si_2 which has eluded a satisfactory

explanation for almost 25 years. Common threads are the interplay of localized and itinerant electron states at various energy scales and the physical complexity resulting from the coexistence and competition between different kinds of order involving charge, orbital, spin and lattice degrees of freedom. Selective tuning of the properties can be achieved by changing chemical compositions or by varying the external conditions through pressure, temperature and magnetic fields. Trapped ultracold atoms provide a unique opportunity to study a Fermi gas with effective spin larger than $1/2$ under extremely pure conditions. The properties studied in atomic gases are closely related to those studied in solid materials, such as phase separation, bound states and superfluidity. Spin-orbit effects can be optically induced into atoms and varied in a controlled manner. In particular, for one-dimensional traps mathematically exact solutions and controlled approximations are available. Field theoretical methods to be employed in all projects are renormalization groups, slave bosons, Schwinger bosons, bosonization, the quantum inverse scattering method and Bethe's Ansatz, wherever applicable.

FY 2014 HIGHLIGHTS

(1) A two electron pocket model including Umklapp processes (the nesting vector is commensurate with the lattice) to allow the transfer of pairs of electrons between the pockets was studied. This model is able to generate a superconducting dome surrounding the quantum critical point due to antiferromagnetic fluctuations, without destroying the crossover from the non-Fermi liquid to the Fermi liquid regime. (2) The NMR relaxation in the strong topological Kondo insulator SmB_6 has been investigated. For a clean surface the Landau quantization of the surface states gives rise to highly degenerate discrete levels and the relaxation rate is not Korringa-like. In the dirty limit the Landau levels are broadened and $1/T_1$ is Korringa-like. (3) The high-field, high-frequency electron spin resonance (ESR) spectra of $\text{Nd}_3\text{Ga}_5\text{SiO}_{14}$ has been interpreted in terms of spin-cluster excitations. (4) The threshold singularities of a one-dimensional gas of fermions with spin S interacting via an attractive δ -function potential have been studied using Bethe's Ansatz and field-theoretical methods.

Theoretical Studies in Very Strongly Correlated Matter

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PROGRAM SCOPE

The goal of this program is to formulate an analytical understanding of the dynamics of very strongly interacting Fermi systems, widely recognized as a 'hard-problem' in Condensed Matter Physics. The program has a strong link to experimental results on ARPES (angle resolved photoemission) line shapes, as well as transport quantities such as the resistivity, Hall constant and thermopower of correlated electron systems. The PI has recently put forward a formalism, termed the extremely correlated Fermi liquid (ECFL) theory, that manages to circumvent several difficult aspects of the strong correlation problem. It leads to controlled and quantitative calculational schemes. At the present state of development, self-consistently reliable results have been found in the somewhat over-doped hole density regime. In the ECFL formalism, the original problem is replaced by a perturbation type problem, where the small parameter λ lies between 0 and 1. Here λ is related to the density of double occupancy.

This latter problem can be treated systematically to successive orders in λ , so that one can build up progressively better approximations. One can use the skeleton graphs expansion for the Greens functions, and in future applications, it is planned to use Monte Carlo methods to sum this series to high orders. This theoretical approach is valid for many models of contemporary interest, including the large U Hubbard model and the t-J model, as well as the single impurity Anderson model. The program also involves calculation of the frequency dependent Greens functions at high T, by computer aided series expansions, and to match this with the analytical theory. For this purpose, development of new algorithms for computing the series for the dynamical Greens function and density-spin density correlation functions to high order in inverse temperature are being developed.

FY 2014 HIGHLIGHTS

We completed two benchmarking projects recently, comparing the new theory with exact results for the single impurity Anderson model and the infinite dimensional strong coupling Hubbard model. In both cases we found that the calculated Z (wave function renormalization) of the lowest order expansion becomes inaccurate for low hole density $\delta \leq 0.25$. However, upon scaling the frequency with the computed Z factor, the ECFL theory and the (similarly scaled) exact results for both of these models agree remarkably well at essentially all densities near the Fermi level. A significant result is that the particle hole asymmetry predicted by the ECFL theory is confirmed quantitatively in the exact results in both models. This asymmetry has been argued by the PI to be central to understanding the ARPES line shapes, so that we have now independent theories that agree in this regard. Our earlier work shows that this also agrees with the experimental data on Cuprate superconducting materials in the appropriate regime. In follow up projects, we have recast the new formalism in much simpler terms than the original presentation, avoiding the Schwinger equations formalism altogether. This is based on the new result that Gutzwiller projected electrons can be represented in terms of usual Fermions, through a mapping that parallels the Dyson-Maleev mapping, where one expresses spins in terms of (regular) Bosons. A path integral formulation of this problem was found. Another result published is a purely diagrammatic method for the (above mentioned) λ expansion to arbitrary orders, analogous to the Feynman rules. This expansion is essential for applying Monte Carlo resummation techniques. Another result published by our group is a computer generated high temperature series for the dynamical one particle Greens function to 8th order in the hopping parameter, earlier results stop at the 4th order.

Novel Fractional Quantum Hall and Quantum Spin Hall Effects in Interacting Systems

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Funding:	\$110,000 (2014)

PROGRAM SCOPE

The research in this program involves theoretical (numerical) study of the correlated topological physics in strongly interacting systems. We study and determine the quantum phase diagram for such systems and the characteristic topological and transport nature of the new emerging quantum phases with topological order and fractionalized quasi-particles. In our computational approach, we develop novel

numerical algorithm for detecting and characterizing new topological phase, entanglement spectrum, and the topological nature and statistics of the quasi-particles in these systems. We have focused on a few related topics in strongly correlated systems including: (a) The fractional quantum spin Hall effect (FQSHE) in topological bands without a magnetic field and quantum phase transition; (b) The space time emergent super-symmetry in the edge state of topological superconductor; (c) Extracting Modular matrix through minimum entangled states to identify different topological phases; (d) Theoretical discovery of the chiral spin liquid and quantum phase diagram for frustrated magnetic systems based on computational method developed in the past a few years.

FY 2014 HIGHLIGHTS

The research in this program involves theoretical (numerical) study of the correlated topological physics in strongly interacting systems. We have focused on a few related topics in strongly correlated systems including: (a) The fractional quantum spin Hall effect (FQSHE) in topological bands without a magnetic field and quantum phase transition; (b) The space time emergent super-symmetry in the edge state of topological superconductor; (c) Extracting Modular matrix through minimum entangled states to identify different topological phases; (d) Theoretical discovery of the chiral spin liquid and quantum phase diagram for frustrated magnetic systems based on computational method developed in the past a few years. Density Matrix Renormalization Group (DMRG) simulations of the nontrivial quantum phase transition and the space time supersymmetry (SUSY): We explore the novel feature of the quantum phase transition for topological superconductors in the presence of spontaneous breaking of the time-reversal symmetry (TRS). In contrast to ordinary symmetries, super-symmetry interchanges bosons and fermions. The topological states themselves may be interpreted as arising from spontaneously broken super-symmetry, indicating a deep relation between topological phases and SUSY. We demonstrate the fractional central charge and scaling law of spin correlations to establish the super-symmetry numerically. We also develop computational method to identify and characterize quantum states with topological order: Following theoretical proposal, we develop numerical methods of obtaining minimum entangled states (MES) and extracting the modular matrix to characterize the topological order of quantum systems. Very recently, we generalized such a method to larger scale simulation based on DMRG calculations. By studying two coupled fractional Chern (FC) insulators, we find a new route to realize non-abelian quantum Hall effect (QHE) state in strongly coupled bilayer systems.

Many-Body Theory of Energy Transport and Conversion at the Nanoscale

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Funding: \$320,000 (2014-2016)

PROGRAM SCOPE

This project addresses the fundamental challenge of understanding quantum systems far from equilibrium, while simultaneously exploring the potential of nanostructured materials for applications in energy-conversion technologies. The main focus of the project is quantum thermoelectrics. The enhancement of thermoelectricity due to electron wave interference in nanostructures is investigated in both the linear and nonlinear regimes. The focus is on increasing the power factor via electron-wave

engineering. This approach can be combined with higher-order nanostructuring designed to minimize the thermal conductance to create revolutionary new types of thermoelectrics with exceptionally high figure of merit ZT . To elucidate the local quantum mechanisms responsible for enhanced thermoelectricity, we investigate local probes of thermoelectricity in quantum systems. The possible relation between thermal eddy currents, nonmonotonic variations of the local temperature, and the enhancement of thermoelectricity are being explored. The nonlinear Peltier effect is studied, with the goal of increasing the efficiency of quantum heat pumps in the nonlinear regime through engineered junction asymmetry. Fundamental research on the nonequilibrium many-body theory of nanostructures is conducted in parallel, to enable the applied research on nanoscale energy conversion. Recently, the PI and collaborators showed that the local temperature of a weakly-driven nonequilibrium quantum system measured by a scanning thermal probe is consistent with the zeroth and second laws of thermodynamics, and agrees with that inferred from an independent electrical noise measurement. This project will investigate under what conditions such a fluctuation-dissipation theorem also applies to the far-from-equilibrium case, and to what extent the local temperature so defined is consistent with the laws of thermodynamics. The effect of coarse graining (or measurement resolution) will also be investigated.

FY 2014 HIGHLIGHTS

A theory of local temperature measurement of an interacting quantum electron system far from equilibrium via a floating thermoelectric probe is developed. It is shown that the local temperature so defined is consistent with the zeroth, first, second, and third laws of thermodynamics, provided the probe-system coupling is weak and broad band. For general probe-system couplings, the local temperature obeys the Clausius form of the second law and the third law exactly, but there are corrections to the zeroth and first laws that are higher-order in the Sommerfeld expansion. The corrections to the zeroth and first laws are related, and can be interpreted in terms of the error of a nonideal temperature measurement. Moreover, the temperature inferred from an independent electrical noise measurement is shown to be identical to that measured by a floating probe within the leading-order Sommerfeld approximation. Large thermoelectric corrections are predicted for ideal voltage measurements at finite temperature in nonequilibrium quantum systems, up to 24% of the peak voltage in a graphene nanoribbon.

Non-Equilibrium Relaxation and Aging Scaling of Magnetic Flux Lines in Disordered Type-II Superconductors

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Funding: \$150,000 (2014)

PROGRAM SCOPE

Technical applications of type-II superconductors in external magnetic fields require an effective flux pinning mechanism to reduce Ohmic losses due to flux creep and flow. The physics of interacting vortex lines subject to strong thermal fluctuations and point-like or extended disorder has therefore been a major research focus in condensed matter physics. This research aims for a thorough theoretical

characterization of the stochastic fluctuations and out-of-equilibrium relaxation processes of interacting vortices subject to various pinning centers. To this end, a versatile three-dimensional Monte Carlo simulation code and a Langevin molecular dynamics algorithm, both based on an elastic string representation of the magnetic flux lines, are employed to extract steady-state observables and two-time correlation functions. The resulting data represent a detailed study of the dynamical relaxation features towards equilibrium as well as non-equilibrium steady states starting from experimentally realizable initial conditions, encompassing sudden thermal, magnetic field, and driving current quenches. Thus universal and non-universal characteristics in the physical aging and glassy relaxation regimes are explored, and thereby unique dynamical signatures that distinguish samples with point pins and extended correlated defects are identified. Future goals include to quantitatively characterize the associated growing length scale in the system, to propose specific experimental setups amenable to probing the different dynamical regimes, and to stimulate the development of novel tools for material characterization and optimization.

FY 2014 HIGHLIGHTS

Extensive Langevin molecular dynamics simulations have been performed to explore in detail the non-equilibrium aging properties of vortex systems subject to either point-like or columnar defects, when in a previously equilibrated state suddenly the magnetic field is increased or reduced, and correspondingly flux lines are either added or removed from the system. Switching off the vortex interactions, removing the disorder, and separately following the originally present and added vortices resulted in a comprehensive understanding of the ensuing complex relaxation kinetics (manuscript in preparation). A series of numerical experiments was initiated to investigate the relaxation features of driven interacting flux lines from an initial non-equilibrium steady state towards either another driven stationary state, or thermal equilibrium. The Langevin dynamics code was also used to extract flux line segment pinning time distributions at point defects, providing clear evidence for collective pinning behavior (just published in *The Physical Review E*, Dec. 2014). In addition, an effectively two-dimensional Coulomb glass model was utilized to further investigate the structural relaxation processes and associated aging scaling in the Bose glass phase of vortices pinned to columnar defects by means of Monte Carlo simulations (published in *The Physical Review E*, Sep. 2014). Another current project concerns the numerical extraction and analysis of the characteristic length scale associated with coarsening during these relaxation processes. Finally, simple driven model systems known to exhibit logarithmic growth laws have been studied (manuscript in preparation). These projects have involved seven graduate students, who have become familiar with modern computational methods and sophisticated data analysis, and have acquired advanced mathematical tools developed in non-equilibrium statistical mechanics.

Unconventional Metals in Strongly Correlated Systems

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Funding: \$115,000 (2014)

PROGRAM SCOPE

The research seeks to develop a theoretical understanding of non-Fermi liquid metallic behavior and its relationship to superconductivity in correlated electron systems such as heavy electron metals, cuprate superconductors and other materials. The most notorious empirical example of such non-Fermi liquid behavior is in the normal state of the optimally doped cuprates but over the past decade has been demonstrated in a number of non-cuprate materials. A striking example is heavy electron materials on the verge of a quantum phase transition to magnetism. Superconductivity is often optimized when the departure from Fermi liquid behavior in the 'normal' state is strongest. The proposed project will explore the nature of the electronic excitations of a non-fermi liquid and its relationship with superconductivity. The PI and his group are currently developing controlled methods to study the emergence of superconductivity out of non-fermi liquid normal states using field theoretic expansion methods combined with renormalization group ideas. In the future he will also explore phenomenological models to understand the feedback of superconducting fluctuations on the normal state excitations and their role in producing non-fermi liquid properties. Another project focuses on studying the novel surface and bulk properties of strongly correlated topological insulators. Other projects are the effects of disorder on various correlated ordered states such as spin density wave metals or pair density wave superconductors.

FY 2014 HIGHLIGHTS

(1) Superconductivity and non-fermi liquid metals: Quantum criticality is often implicated for both the breakdown of Fermi liquid theory and the superconductivity seen in many correlated metals. In a paper (under review in PRB) we described progress in studying these issues theoretically in two dimensional metals pushed close to the onset of nematic order which breaks crystal rotation but not translation symmetries. A theoretical framework for such a quantum critical point was developed earlier in my group (D. Mross, J. McGreevy, H. Liu, and T. Senthil, Phys. Rev. B 82, 045121 (2010)) but that work did not address possible instabilities toward superconductivity. Recently, we reported controlled calculations within this framework and showed that superconductivity is strongly enhanced near such quantum critical points. This is one of the few, and hence valuable, examples where the idea that quantum criticality can enhance superconductivity can be theoretically analyzed reliably and given firm foundation. The methods developed also enabled solving a different class of problems - namely the quantum phase transition between the composite Fermi liquid state in the half-filled Landau level and the Moore-Read non-abelian quantum Hall state. Closely related is the phase transition between two different kinds of popular quantum spin liquids (the spinon Fermi surface state and a different 'paired' version). (2) Strongly correlated three dimensional electronic topological insulators: A fundamental open problem in condensed matter physics is how the dichotomy between conventional and topological band insulators is modified in the presence of strong electron interactions. In a paper (published in Science) I, together with my student C. Wang and former MIT student A. Potter showed that there are 6 new electronic topological insulators that have no non-interacting counterpart.

Orbital-Free Quantum Simulation Methods for Application to Warm Dense Matter

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Funding: \$255,000 (2014)

PROGRAM SCOPE

Development and exploratory use of orbital-free forms of free-energy density functional theory (DFT) is the focus. Motivation is the pressing need for affordable, reliable simulations of warm dense matter (WDM). WDM is important experimentally for planetary interiors, hyper-velocity impacts, heavy-ion beam experiments, and dynamically accessed high-pressure regimes (e.g., pathway to inertial confinement fusion). Predictive computational WDM characterization is important because of limited experimental diagnostic access. A major challenge is that WDM is a mixture of atoms, ions, and free electrons. Powerful zero-temperature quantum mechanics techniques for electronic structure are stressed severely to treat WDM while standard plasma methodology omits crucial quantum effects. Current best practice is *ab initio* molecular dynamics (AIMD) with the electron forces on the ions from DFT. Ordinarily this is in the Kohn-Sham (KS) form, which causes a computational bottleneck. KS calculations scale up in cost as the cube of the number of occupied KS states, a very large number at WDM temperatures (T up to 300,000 K or more). The orbital-free formulation, depending only on the electron density, eliminates this bottleneck. But the historic orbital-free approaches (Thomas-Fermi and refinements) cannot describe the condensed matter physics (including bonding) crucial to WDM. This project thus focuses on developing reliable, non-empirical free-energy density functionals for (i) non-interacting kinetic energy and entropy, and (2) exchange correlation free energy, with emphasis on accuracy and generality of applicability. We also develop and publish numerical techniques and software, including downloadable open-source orbital-free AIMD software, projector augmented wave data sets and pseudo-potentials for WDM. To our knowledge we are the only academic group in the world devoted primarily to finite-T DFT.

FY 2014 HIGHLIGHTS

1. We developed the first wholly un-empirical exchange-correlation (XC) free-energy density functional in the local density approximation. It depends only on first principles Monte Carlo (MC) data and is constructed to be smooth with well-behaved derivatives over the entire density-temperature regime of warm dense matter (WDM). Derivation was by systematic thermodynamic analysis of the MC data. This is the long-missing finite-T extension of the Perdew-Zunger and Vosko-Wilk-Nussair T=0 functionals (1981!). Paper: Phys. Rev. Lett. 112, 076403 (2014).
2. Our orbital-free non-interacting free-energy functionals [Phys. Rev. B 88, 161108(R) (2013)] and the new XC free-energy functional were implemented in the PROFESS orbital-free code. In turn it was interfaced to the Quantum-Espresso electronic structure package to provide orbital-free DFT driven *ab-initio* molecular dynamics (AIMD) simulations of WDM. Released under GNU GPL, the software is downloadable from www.qtp.ufl.edu/ofdft. Paper: Computer Phys. Commun. 185, 3240 (2014).
3. We began studies now well underway of (a) liquid-vapor phase transitions in Al with our new OFDFT functionals in AIMD; (b) Deuterium phase diagram with OFDFT functionals driving path-integral molecular dynamics; (c) Relationship of grand-canonical ensemble (in which free energy DFT is derived) and canonical ensemble (in which actual calculations must be done), (d) application of classical maps.
4. We organized 4 sessions of Sanibel Symposium 2014 on *ab initio* simulations at extreme conditions, had 3 visitors (Bonitz, Lutsko, Segev), saw 'Frontiers and Challenges in Warm Dense Matter' (Springer) appear, and gave invited talks at M4 (Canada) by Chakraborty, Sanibel 2014 by Karasiev, HarrisFest (Mexico) by Dufty, Runge, and

Trickey; and Interat. Materials Conf. (Mexico) and WATOC (Chile) by Trickey along with several others. 5. See www.qtp.ufl.edu/ofdft for the complete record.

Quantum Simulations of Orbitally Controlled Physics and Nanoscale Inhomogeneity in Correlated Oxides

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Funding: \$360,000 (2014-2016)

PROGRAM SCOPE

I will focus on both metal-insulator and superconductor-insulator transitions driven by disorder in conventional s-wave superconductors. My aim is to investigate the effect of emergent nanoscale inhomogeneity on local electronic structure and dynamical susceptibilities that could be measured by various scan probes.

FY 2014 HIGHLIGHTS

We calculated the dynamical conductivity across the superconductor-insulator transition (SIT) driven by tuning the ratio of the charging energy to the Josephson energy. We showed that there is a threshold in absorption at low frequencies, well below the pair breaking scale, associated with the amplitude or Higgs mode. And most importantly, we found that the Higgs mode vanished at the quantum critical point with a universal conductivity. We further included the effects of disorder and found that it leads to an expanded quantum critical region with a different critical conductivity, indicating a change in the universality class.

Nonequilibrium Thermodynamics in Magnetic Nanostructures

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PROGRAM SCOPE

The nascent field of spin caloritronics addresses emergent out-of-equilibrium phenomena in thermally-biased magnetic systems. This proposal focuses on the geometric gauge fields and related geometric and topological aspects in the interactions between collective and itinerant degrees of freedom (associated with diverse magnetic orders), the former encoding “memory” (i.e., slow variables) and imprinting evolving geometrical spin textures, while the latter transmitting “signals” through these curved backgrounds. Energy and spin (angular momentum) are at the core of the investigation, bringing about phenomenological framework based on conservation laws, hydrodynamic continuity, magnetic order, symmetries, and dynamic reciprocities. The main objective of the proposal is to identify and study

self-organized nonlinear phenomena and dynamical phase transitions in thermally driven magnetic systems. Particular attention is paid to low-dissipation, mainly, insulating systems, where quantum statistics, coherence, and correlations play an important role. The PI believes the ideas developed as a result of this project may find wide applications within nonequilibrium phenomenology of magnetism, in the era ushered in by a range of experimental tools and novel phenomena (such as spin pumping, spin Hall effect, and spin Seebeck effect) to thermally agitate and probe complex magnetic heterostructures. The relativistic electronic correlations, which are at the heart of the relevant microscopies, will be playing a central role.

FY 2014 HIGHLIGHTS

The main accomplishment for the project within fiscal year 2014 is represented by the preprint titled “Interfacial Spin and Heat Transfer between Metals and Magnetic Insulators.” In this work, we study the role of thermal magnons in the spin and heat transport across a normal-metal/insulating-ferromagnet interface, which is beyond an elastic electronic spin transfer. Using an interfacial exchange Hamiltonian, which couples spins of itinerant and localized orbitals, we calculate spin and energy currents for an arbitrary interfacial temperature difference and misalignment of spin accumulation in the normal metal relative to the ferromagnetic order. The magnonic contribution to spin current leads to a temperature-dependent torque on the magnetic order parameter; reciprocally, the coherent precession of the magnetization pumps spin current into the normal metal, the magnitude of which is affected by the presence of thermal magnons.

Charge and Spin Dynamics in Bulk and Heterostructured Dilute Magnetic Semiconductors

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Funding: \$105,000 (2014)

PROGRAM SCOPE

This project studies the dynamics of collective excitations of the itinerant carriers in dilute magnetic semiconductors (DMS). Plasmon-type excitations are not only of interest in their own right, but are ideal for testing microscopic models for the carrier dynamics in semiconductors. The following problems will be studied: (1) Plasmons and spin waves in bulk DMS. Plasmons in p-type semiconductors are usually strongly Landau damped, but there are indications that it may be possible to find plasmon modes outside the particle-hole continua. Such modes will be sensitive to details of disorder broadening, such as correlated versus random disorder, or a self-consistent treatment of disorder scattering. We will also extend our formalism to study Stoner excitations and spin waves in ferromagnetic DMS. (2) Spin Coulomb drag beyond the local approximation. The spin Coulomb drag (SCD) is an intrinsic effect which represents an ultimate limitation for spintronics. The linewidth of intersubband spin plasmons in quantum wells represents a new and purely optical way to measure the SCD effect, using inelastic light scattering. We propose a new and more accurate way of calculating the SCD in quantum confined systems, beyond the usual local approximation. A detailed analysis of light scattering experiments, including Rashba and Dresselhaus spin-orbit coupling, will be performed. (3) Collective intersubband excitations in semiconductor heterostructures. We will extend our approach for charge and spin

dynamics in DMS to lower-dimensional and quantum confined systems, with the goal of studying collective intersubband excitations in n- and p-type systems. In particular, changes of the line shape as the system undergoes a ferromagnetic transition will reveal how the carrier dynamics in DMS is influenced by disorder, band-structure, spin-orbit coupling, and many-body effects.

FY 2014 HIGHLIGHTS

During the period of October 2013 to September 2014 we have focused on two projects, and have made major progress in both of them. The first project was carried out by my postdoc Mehul Dixit (who left my group on October 1 for a position in industry), and involved the theoretical analysis and numerical simulation of spin-flip waves in CdMnTe quantum wells. In the presence of magnetic fields, this material is a superparamagnet, which leads to a strong spin splitting of the subbands. The spin-flip wave is modulated due to Rashba and Dresselhaus spin-orbit coupling, which is amplified by electronic many-body effects. We have published a joint experimental-theoretical study earlier [Phys. Rev. B 87, 1221303 (2013)] together with the group of Florent Perez in Paris. We during the past year we have carried out an in-depth theoretical analysis, with many analytical and numerical results. This work will soon be ready for publication. The collaboration between PI Ullrich and the group in Paris has intensified over the past year; next summer, the PI will spend a month in Paris, supported by a local grant. The second project was carried out by my graduate student Shahrzad Karimi, and has just been accepted for publication in Phys. Rev. B. It is a study of the three- to two-dimensional crossover in time-dependent density-functional theory (TDDFT). The most popular density functionals (LDA and GGA) are known to breakdown in the ground state when the system becomes more and more confined in 2D, and we have now shown, for the first time, when and how the corresponding breakdown occurs in the dynamical regime. We find that semilocal xc functionals collapse for quantum well widths close to the 2D Wigner-Seitz radius (which means that they will still work for many typical quantum wells). On the other hand, orbital functionals will cross over correctly from 3D to 2D.

Computational Studies of Hydrogen Interactions with Storage Materials

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Funding: \$140,000 (2014)

PROGRAM SCOPE

We are conducting computational studies with the goal of developing new insights for hydrogen interactions with materials. We use state-of-the-art density functional calculations and address energetics and electronic structure. We pursue new computational approaches, such as the incorporation of van der Waals interactions within density functional theory. Our recent work has focused on borohydrides, LiH, layered compounds such as MoS₂ and MoO₃, and perovskite-structure oxides. For hydrogen storage materials our results provide direct insight into the processes of hydrogen uptake and release, and help in developing guidelines for designing storage media with improved storage capacity and kinetics. We propose atomistic mechanisms for the material's decomposition that involve mass transport mediated by native defects. In addition to the hydrogen storage aspect, we view our results from the perspective of other applications, including electrochromism and photochromism,

as well as proton conduction. Hydrogen can be incorporated in high concentrations in materials that crystallize in the perovskite crystal structure, such as rare-earth or transition-metal doped BaZrO₃ and SrZrO₃. These materials not only display higher hydrogen solubility than other metal oxides, but also proton conductivity at elevated temperatures. Proton conductors based on perovskites are used in solid oxide fuel cells. We are focusing on building an understanding of the interactions between hydrogen, acceptor dopants, and native point defects. This will help in designing novel electrolyte materials. Our overall goal is twofold: (1) to develop guidelines for designing materials with improved properties; and (2) to generate new fundamental knowledge, for instance, about mechanisms that govern ionic transport in insulators.

FY 2014 HIGHLIGHTS

(1) Role of native defects in the decomposition of Li₄BN₃H₁₀ Li₄BN₃H₁₀ releases greater than 10 wt% hydrogen when heated. Still, its practical application is limited due to the cogeneration of ammonia. Based on first-principles results we have proposed an atomistic mechanism for the decomposition that involves mass transport mediated by native defects. The release of NH₃ is associated with the formation and migration of negatively charged hydrogen vacancies inside the material, and it can be manipulated by the incorporation of transition-metal impurities. (2) Van der Waals interactions in density functional calculations A number of methods have been proposed to include van der Waals interactions within density functional theory (DFT). We have compared the performance of several of these functionals specifically for describing the structural and electronic properties of MoS₂ and MoO₃, materials at the focus of our project. Our conclusion is that the combination of the semiempirical Grimme D2 method with the hybrid functional HSE06 leads to a very good description of structural and electronic properties. (3) Properties of layered compounds: MoS₂ and MoO₃ We have used our methodology for calculating properties that are essential for applications but still unknown or controversial. We have traced the evolution of the band structure as a function of the number of layers in MoS₂, starting from a monolayer, which has a direct gap, to the bulk material, which has an indirect gap. These findings are analyzed in terms of the orbital composition of the valence- and conduction-band edges at the various high-symmetry points in the Brillouin zone. We challenge the common belief that the change in band gap of MoS₂ as a function of the number of layers is due to quantum confinement. We have also performed calculations of the elastic constants in bulk MoS₂, and investigated the effects of hydrostatic pressure, shedding light on experiments.

Dynamical and Non-Equilibrium Effects in Higher-Order and Pump and Probe X-Ray Scattering

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Funding: \$130,000 (2014)

PROGRAM SCOPE

The aim of this project is to develop theoretical tools that allow a better understanding of X-ray experiments performed at the nation's light sources. X-ray spectroscopy is entering a new era with an increased emphasis on the study of dynamics and nonequilibrium effects that is essential for understanding phenomena relevant to solving the challenges in energy and information technology. The

first focus is centered on the study of the local X-ray scattering amplitude of a system excited away from equilibrium by, for example, a femtosecond optical or terahertz pulse. Typical examples of such effects are charge-transfer and spin crossover phenomena. When studying finite-size systems, the nonequilibrium dynamics can be treated quantum mechanically by including the coupling to local vibronic modes, dissipation and the effects of loss of coherence. The second focus is on larger systems and the ultrafast melting of long-range charge, orbital, spin, and structural order. The research is directed towards creating an understanding of the disappearance of the order as measured by the decrease in X-ray diffraction and resonant elastic X-ray scattering intensities. The effects of coupling between the electronic states and the lattice, orbital degeneracy, and electron count are studied. This provides insight into the conditions for a transition from a local to a collective response and the possible emergence of new phenomena due to correlation effects. Results on model systems are then extended and modified to allow the calculation of X-ray spectroscopies, such as time-dependent X-ray absorption and dichroism and resonant elastic scattering. The project also involves extensive collaborations with experimental groups. Here, the focus has been on the study of strongly correlated materials, such as transition-metal compounds, using X-ray spectroscopic tools that were the focus of the theoretical research in previous funding cycles.

FY 2014 HIGHLIGHTS

Just prior to the start of the year, significant progress was made in the study of the ultrafast phase transitions. Insulator-to-metal transitions have been observed in VO_2 , V_2O_3 , manganites, etc. A model was developed for the ultrafast insulator-to-metal transition in VO_2 following photoexcitation. The model explains several key features, such as a structural bottleneck, coherent structural motion combined with phase shifts in the oscillation, the absence of ultrafast metal-to-insulator transitions, and the need for a critical fluency. The work on photo-induced phase transitions has been continued with the study of charge-order melting. In particular, the focus has been on model systems of 100,000 and more sites to study the nonequilibrium thermodynamics of photoexcited systems. In the past decade, Resonant Inelastic X-ray Scattering (RIXS) has made remarkable progress as a spectroscopic technique. In collaboration with Ken Ahn from New Jersey Institute of Technology and experimentalists from Brookhaven and Argonne National Laboratories, a study was made of resonant inelastic x-ray scattering on single-layered charge, orbital and spin ordered manganites. Good agreement has been found between the theory and experiment, which demonstrates the potential of K-edge RIXS as a probe for the screening dynamics in materials. X-ray scattering is also an important tool in high-pressure studies due to the large penetration depth of the X-rays. An example of such a study is the behavior of vanadium sesquioxide, V_2O_3 , at high pressures. From X-ray Raman scattering, we found that screening effects, which are strong in the corundum phase, become weakened at high pressures. The theoretical calculations indicate that this can be related to a decrease in coherent quasiparticle strength, suggesting that the high-pressure phase is likely a critical correlated metal, on the verge of Mott-insulating behavior. This work was an Editor's Selection in Physical Review Letters.

Self-Healing Nanomaterials: Multimillion-Atom Reactive Molecular Dynamics Simulations

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Funding: \$180,000 (2014)

PROGRAM SCOPE

This project focuses on self-healing nanomaterials capable of sensing and repairing damage in harsh chemical environments and in high temperature/high pressure operating conditions. We perform petascale simulations to study self-healing processes in anticorrosion coatings for metals and in ceramic nanocomposites.

FY 2014 HIGHLIGHTS

We enabled an unprecedented scale of quantum molecular dynamics (QMD) simulations through algorithmic innovations. A lean divide-and-conquer density functional theory algorithm significantly reduces the prefactor of the $O(N)$ computational cost. The resulting parallel efficiency was 0.984 on 786,432 IBM Blue Gene/Q cores for a 50.3 million-atom system. The time-to-solution was 60-times less than the previous state-of-the-art, owing to high floating-point performance (50.5% of the peak). QMD simulations involving 16,661 atoms reveal a novel nanostructural design for on-demand hydrogen production from water using Al particles. We found that orders-of-magnitude faster reactions with higher yields can be achieved by alloying Al particles with Li. A key nanostructural design is identified as the abundance of neighboring Lewis acid-base pairs, where water-dissociation and hydrogen-production require very small activation energies. These reactions are facilitated by charge pathways across Al atoms that collectively act as a 'superanion', and a surprising autocatalytic behavior of bridging Li-O-Al products. Furthermore, dissolution of Li atoms into water produces a corrosive basic solution that inhibits the formation of a reaction-stopping oxide layer on the particle surface, thereby increasing the yield. These mechanisms not only explain recent experimental findings, but also predict the scalability of this technology at industrial scales. We also examined water confined in nanoporous silica using molecular dynamics simulations. The simulations reveal intermixed low-density water and high-density water and with distinct local structures in nanopores of silica. The simulations also show dynamic heterogeneities in nanoconfined water. The temporal decay of cage correlation functions is well described by stretched exponential relaxation. The exponent has a unique value, which agrees with an exact result for diffusion in systems with static, random traps.

Disorder and Interaction in Correlated Electron Systems

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Funding: \$480,000 (2014)

PROGRAM SCOPE

This project studies the emergent quantum electronic states, low energy excitations, and unconventional superconductivity in correlated electron materials. The first part investigates the microscopic origin of superconductivity in Fe-pnictide superconductors. A novel mechanism of superconductivity driven by charge and orbital fluctuations will be explored. A microscopic theory will be developed for the spin state transition induced by the large Hund's rule coupling to address the

substantial variations of the ordered moments, the highly incoherent metallic state with the anomalous temperature dependence of the spin-susceptibility, the orbital and the electron/spin nematic order. The second part studies two central unresolved problems in high- T_c cuprate superconductors: What controls T_c and what is the origin of the normal state pseudogap? Guided by new experimental findings, the program will study how the out-of-plane atomic and electronic structure affects the electronic states in the CuO_2 plane and the superconducting (SC) transition. The project investigates the scenario where the pseudogap state originates from a symmetry breaking phase transition of incommensurate, d-wave bond density wave order. The effects of electronic disorder resulting in the valence bond glass state will be investigated. The third part aims at advancing the theoretical understanding of the Mott transition. The challenge of the strong correlation problem is a consistent description of both the coherent quasiparticles and the incoherent excitations. The project proposes that the crucial ingredient uniting these disparate ideas of Brinkman-Rice-Gutzwiller and Hubbard is the binding between doublons and holons. A microscopic theory will be developed to describe doublon-holon binding in the Hubbard model and applied to study the Mott transition, magnetism, and spin-liquid phases on different lattices. The notion of an electron-fractionalized antiferromagnetic (AF*) phase without coherent quasiparticles will be investigated.

FY 2014 HIGHLIGHTS

Mott Transition: Stoner and Fractionalized Antiferromagnet in the Hubbard model The Hubbard model is the “Standard Model” of correlated materials and the Mott transition is the most important Hallmark and the paradigm of the strong correlation problem. Understanding the Mott transition and its interplay with magnetism is a central unresolved problem of the “Standard Model”. We have developed new ideas, new techniques, and realized new physics beyond those obtainable in the dynamical mean field theory. We found that the binding between doubly occupied (doublon) and empty (holon) sites governs the incoherent Mott-Hubbard excitations and plays a key role in the Mott transition. We construct a new saddle-point solution with doublon-holon binding in the Kotliar-Ruckenstein slave-boson functional integral formulation of the Hubbard model. On the half-filled honeycomb lattice and square lattice, the ground state is found to exhibit a continuous transition from a paramagnetic semimetal/metal to an antiferromagnetic (AF) ordered Slater insulator with coherent quasiparticles, followed by a Mott transition into an electron-fractionalized AF* phase where a charge gap opens and electrons fractionalize into separate spin and charge elementary excitations without coherent quasiparticles. Such a phase structure appears to be generic for bipartite lattices without magnetic frustration. We showed that doublon-holon binding unites the three important ideas of strong correlation: coherent quasiparticles, incoherent Hubbard bands, and deconfined Mott insulator.

Strong Correlation DMRG and DFT

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Funding: \$237,322 (2014)

PROGRAM SCOPE

We are successfully comparing one of the most popular electronic structure methods, density functional theory (DFT), with the extremely precise density matrix renormalization group (DMRG). DFT has two quite different facets: an 'in principle' aspect, in which DFT is exact but impractical to compute, and a 'common approximations' aspect, where an approximate functional is assumed, which may have uncertain accuracy. The 'common approximations' approach has proved extremely useful for a vast array of systems where correlations are not too strong. Improving these approximations for strong correlation is an important goal for this field. For one dimensional systems, DMRG provides essentially exact results. With these results, we can explore both the 'in principle' and 'common approximations' aspects of DFT. For three dimensions, DMRG becomes impractical, except in a modest basis for moderate sized molecules. We have developed and continue to develop 1D model systems constructed so the lessons we learn about DFT for the 1D model apply to the realistic 3D world. For example, a key issue for DFT is finding accurate gaps. We find that for strongly correlated 1D 'pseudosolid' model systems, the gaps in DFT do not open properly in 1D, just as in 3D. We have been able to calibrate correlations energies in our 1D systems to that they are very similar in size, per atom, to 3D. Finding the exact solution with DMRG allows us to back calculate exact DFT quantities and this has led us to some surprising conclusions. Most recently we proved that DFT can always be guaranteed to converge if one uses the exact functional (Physical Review Letters 111, 093003, 2013). But a variety of work can still be performed with these comparisons. We will explore in the upcoming months common problems and potential fixes for regular DFT calculations.

FY 2014 HIGHLIGHTS

The principle achievement of the 2014 FY is the publication of a comprehensive account of convergence in density functional theory, 'Kohn-Sham calculations with the exact functional', in Physical Review B (90, 045109). This publication has been well received garnering an Editor's Choice award and high praise from the community at both the 2014 March Meeting, where T.E. Baker presented on the findings as well as the Institute of Pure and Applied Mathematics's summer school on density functional theory (also presented by T.E. Baker). In general, we have received reaction that the paper has been hailed as a solid account of issues many groups face. Several more exciting projects are underway. We are preparing to submit two articles as next steps in our work to explore DFT with exact conditions provided by DMRG. First, we have developed a simplified interaction in one dimension based on an exponential that we will submit to Physical Review A. It is natural to implement such an interaction into DMRG and decreases computational times in other calculations as well. It is hoped that future works working in one dimension will use this interaction as it converges to a high accuracy quickly in both DMRG and DFT systems owing to the short decay length. Remarkably, the energetics and properties of pseudo-atoms in this system are nearly exactly what is expected from the more commonly used, but more difficult to converge, soft-Coulomb interaction. We will use it to explore the band gap problem and are preparing a full account for publication on that topic right now. The second paper we are preparing is a proof of principle that machine learning can learn the fundamental universal functional guaranteeing that DFT has a well defined form. This is a ground-breaking study targeted for Physical Review Letters. The consequences for electronic structure calculations are the first realization of the longstanding dream of determining a fully orbital free DFT.

Thermodynamics and Kinetics of Phase Transformations in Energy Materials

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Funding: \$780,003 (2014-2016)

PROGRAM SCOPE

In many areas of sustainable energy (batteries and supercapacitors, solar fuel oxides, hydrogen storage, etc.), functional materials are engineered to undergo phase transformations. Both thermodynamic and kinetic factors need to be taken into account when designing new materials. Thermodynamics sets the necessary-but-not-sufficient conditions for the suitability of a particular material in a given application. High-throughput computation of the total (free) energies can serve as a useful thermodynamic screen for potential materials, but the potential configuration space is too vast to be amenable to an exhaustive search. The kinetics of transformations are often very difficult to assess at a mechanistic level, since so many processes could be rate limiting. The complexity of these phenomena makes computational design difficult, not least due to the lack of suitable theoretical methods and computational tools. To address the needs of the next stage of the Materials Genome Initiative, we propose to develop systematic, quantitatively accurate first-principles methods to address two important problems: (i) predict and optimize the thermodynamics of phase transformations over a large composition and structure space, and (ii) model the kinetics of nucleation and mass transport in solid-state chemical reactions. Task (i) will be addressed by combining state-of-the-art statistical algorithms for uncovering hidden relations in large computed data sets with high-throughput computation of reaction enthalpies and novel DFT-based crystal field and compressive sensing lattice models for predicting electronic and configurational entropies. Task (ii) will be addressed by developing predictive high-throughput framework for defect energetics and diffusivity calculations, combined with symmetry-adapted structure prediction methods.

FY 2014 HIGHLIGHTS

Accomplishments (and publications, where applicable) have fallen into the following research areas: [1] H. A. Hansen and C. Wolverton, 'Kinetics and Thermodynamics of H₂O Dissociation on Reduced CeO₂(111)', J. Phys. Chem. C 118, 27402 (2014). [2] M. Aykol and C. Wolverton, 'Local environment dependent GGA+U method for accurate thermochemistry of transition metal compounds', Phys. Rev. B 90, 115105 (2014). [3] High-Throughput Discovery of Perovskites for Thermochemical Water Splitting - Theoretical investigation of self-stopping mechanism in evaporative thinning approach for 2D materials Huang, Y.K.; Cain, J. D.; Peng, L.; Hao, S.; Chasapis, T.; Kanatzidis, M. G.; Wolverton, C.; Grayson, M.; and Dravid, V. P., "Evaporative Thinning: A Facile Synthesis Method for High Quality Ultrathin Layers of 2D Crystals", ACS Nano 8, (2014) 10851. [4] Stability of monolayer semiconducting transition metal dichalcogenide alloys and band bowing [5] Phase transformation kinetics in lithium amide and lithium alanates

Proximity Phenomena in Graphitic Nanostructures: Theoretical Studies

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Funding: \$50,000 (2014)

PROGRAM SCOPE

The objective of this project is to investigate Casimir/van der Waals interactions and thermal exchange processes involving graphitic nanostructures. The unique electronic structure, optical response and dimensionality give rise to a series of interesting effects relying on the long-ranged dispersive interaction involving graphene nanostructures. Our studies contributed significantly to the understanding of the underlying interplay between quantum mechanical and thermal effects that help us find new opportunities to tailor Casimir/vdW interactions in terms of the strength, distance and temperature dependence, and even sign. The related phenomenon of electromagnetic heat exchange was also studied in depth showing heat management pathways by controlling the properties of graphene systems. Our work shows the limitations and advantages of using graphene systems especially at the near-field regime of operation.

FY 2014 HIGHLIGHTS

Several important results were achieved in this period. More specifically, a microscopic approach of near-field heat transfer in graphitic nanostructures was presented showing features not accessible via an effective medium theory. Graphene transverse electric models can also be enhanced in a near-field exchange process utilizing metamaterial composites. Depending on the particular metamaterial, it is suggested that the role of chemical potential and scattering rates of graphene can be probed in near-field radiation. Van der Waals and Casimir interactions between graphitic systems were also studied with the purpose of developing effective theoretical techniques for an adequate description. More specifically, a Lifshitz-like approach was developed for graphene nanoribbons as a prototype of quasi-1D systems interacting via a van der Waals force. Furthermore, the zero-point summation method was extended to be applicable to planar and spherical systems characterized by a constant conductivity motivated by the fact that under certain conditions graphene can be described by a constant conductivity. A series-expansion method was also presented for graphitic systems for which the dilute regime is applicable. This approach is especially attractive as it enables one to deal with edge effects and nontrivial geometries in a transparent way.

EARLY CAREER: Quantum Mechanical Simulations of Complex Nanostructures for Photovoltaic Applications

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Funding: \$150,000 (2014)

PROGRAM SCOPE

In this proposal, the PI will first address the excited-state problem within the DFT framework to obtain quasiparticle energies from both Kohn-Sham (KS) eigenvalues and orbitals; and the electron-hole binding energy will be computed based on screened Coulomb interaction of corresponding DFT orbitals. The accuracy of these approaches will be examined against many-body methods of GW/BSE and quantum Monte Carlo (QMC). The PI will also work on improving the accuracy and efficiency of the GW/BSE and QMC methods in electronic excitation computations by using better KS orbitals obtained from orbital-dependent DFT as inputs. These new developments will then be applied to investigate a chosen set of complex nanostructures that have great potential for opening new routes in designing materials with improved transport, electronic, and optical properties for Photovoltaic (PV) and other optoelectronic usages: (1) Hybrid interfaces between materials with distinct electronic and optical properties, such as organic molecules (conjugated polymers, e.g. P3HT) and inorganic semiconducting materials (Si and ZnO). Complicated interface structures, including interface bonding configurations, compositional and geometrical blending patterns, interfacial defects, and various sizes and shapes of inorganic nanomaterials, will be considered for the purpose of understanding the working mechanisms of present organic/nano PV systems and designing optimum interface structures for fast charge separation and injection. (2) Complex-structured semiconducting nanomaterials that could induce charge separation without pn- or hetero-junctions. The new methodology will allow the PI to investigate the performance of realistic semiconducting nanomaterials of internal (impurities, defects, etc.) and external (uneven surface, mechanical twisting and bending, surface chemistry, etc.) complexities on optical absorption and charge transport against charge trapping and recombination.

FY 2014 HIGHLIGHTS

(1) Transitions between Semimetal and Semiconductor in Graphene. We reveal that a semimetal-to-semiconductor transition can be induced geometrically without breaking the sublattice symmetry. For the same patterning periodicity, however, breaking the sublattice symmetry increases the gap, while phase cancellation can lead to a semiconductor-to-semimetal transition in non-Bravais lattices, and the Dirac points move in accordance with the anisotropy induced by the defect. Our GW/BSE calculations reveal large band gap renormalization and giant excitonic effects. In addition, we find that topological phase transition occurs with large bulk gap and small spin-orbit interaction. (2) Band gap engineering of silicon nanowires via twisting. We investigated the effect of twisting on electronic properties of silicon nanowires (Si NWs). As twisting angle increases, E_g increases slightly except for the [111] NW, then it decreases dramatically for the [001] and [011] NWs, while E_g in the [001] NW decreases nearly linearly with twisting angle. Thus our calculations suggest that electronic structures of Si NWs can be tuned by twisting. (3) Tailoring the optical gap of silicon quantum dots for photovoltaic cells. Our first principles analysis indicates that connecting conjugated organic ligands to silicon quantum dots using vinyl connectivity can satisfy both requirements. For a prototype assembly of 2.6 nm dots, we predict that triphenylamine termination will result in a 0.47 eV redshift along with an enhanced near-edge absorption character. Robustness analyses of the influence of oxidation on absorption and of extra alkyl ligands reveal that the control of both factors is important in practical applications. (4) Quasi-particle energies from density functional theory. We have developed the quasiparticle-DFT (QP-DFT) method based on the first-order perturbation theory, whose computational overhead is essentially the same as that of DFT DFT and accurately calculated the fundamental band gap (E_g) by QP-DFT.

Laser-Induced Ultrafast Magnetization in Ferromagnets

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Funding: \$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

Our project focuses on a new frontier in future magnetic recording and fast magnetic storage device using the laser-induced ultrafast demagnetization in ferromagnets. Our goal is to develop a clear understanding of how the laser can demagnetize magnetic samples so quickly. This potentially has a big impact on the future devices.

FY 2014 HIGHLIGHTS

We have made remarkable progresses in the fiscal year 2014. (1) We discovered that pressure can directly affect the demagnetization process in ferromagnetic 3d metals. The stronger the pressure is, the smaller the demagnetization is. The reason for this is that there are several optically accessible bands shifted, which become off-resonant. This can be directly tested experimentally. This result was published in Phys. Rev. B Volume 88, 144425 (2013). (2) For the first time, we crystal-momentum dispersed the ultrafast spin change in fcc Co. This result demonstrates that in contrast to the existing wisdom, the demagnetization is not uniform in any pockets of the Brillouin zone. Instead, some pockets are more strongly excited than others. We develop an animation for the entire demagnetization in the three-dimensional space. This result was published in the prestigious Scientific Reports Volume 4, Article number: 5010 (2014). (3) We finally uncovered the role of the exchange interaction in the laser-induced demagnetization process. Since the beginning of femtomagnetism, it has been hotly debated how an ultrafast laser pulse can demagnetize a sample and switch its spins within a few hundred femtoseconds, but no consensus has been reached. In this paper, we propose that an ultrafast reduction in the exchange interaction by a femtosecond laser pulse is mainly responsible for demagnetization and spin switching. This result was published in Journal of Cond. Matt. Volume 26, 376001 (2014).

Theory of Defects in Electronic Materials

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Funding: \$300,000 (2014)

PROGRAM SCOPE

The goal of this project is to carry out theoretical development for accurate predictions of defects properties in electronic materials, and to perform, in parallel, cutting-edge research in defect physics, such as non-equilibrium doping, deep-level engineering, excited-state properties, and defect-defect

interaction and correlation using first-principles theoretical tools with balanced accuracy and computation efficiency. We employ a comprehensive set of density functional theory (DFT) methods such as the local density approximation (LDA) and generalized gradient approximation (GGA)-based molecular dynamics (MD), the time-dependent DFT (TDDFT), and the hybrid functional methods, and the many-body GW quasiparticle perturbation theory. We examine, for charged defects, the response of the screening charge to the defect and the effects of the artificially introduced compensating jellium background, with the aim of eliminating unphysical interactions. Non-equilibrium doping is an active research topic of high current interest. We will push the frontier of *ab initio* defect study from mainly isolated point defects to strongly interacting defects, e.g., clustering, and from mainly ground-state properties to excited-state properties. We will also explore possible paths to lower dopant ionization energy in ultrawide gap materials. Designing electronic materials with controllable properties is important for the development of economically viable, resource-sustainable, and environmentally friendly energy materials. Such materials are the key to technology breakthroughs in increased energy harvesting, transformation, storage, and utilization efficiencies, which in turn secure U.S. leadership in clean energy technologies, increase U.S. national security, improve U.S. economic prosperity, and increase U.S. global competitiveness.

FY 2014 HIGHLIGHTS

Negatively charged nitrogen-vacancy (NV^-) center in diamond has emerged as a promising system for quantum information. Its promise has inspired unprecedented research interests in optical manipulations of defect states, and has fostered the search for alternative low-cost defect systems. We predict an NV^- -like color center in c-BN, consisting of a substitutional oxygen and an adjacent boron vacancy. It displays most of the interesting properties of the NV^- center, is optically accessible with a zero-phonon line of about 1.6 eV, and shares much of the characteristics of the GC-2 center often observed in c-BN [Phys. Rev. Lett. 113, 136401 (2014)]. Kagome lattices have attracted great attention for understanding the physics of frustration. Spin frustration is expected to yield fascinating exotic physics. Other physical quantities such as electronic orbitals should also show frustration in a Kagome lattice. We proposed a three-dimensional elemental carbon Kagome lattice, whose stability is comparable to C_{60} . Orbital frustration in this system is responsible for the emergence of a direct band gap of 3.43 eV. Both the electron and hole effective masses are comparable to those of Si, while the imaginary part of the dielectric function is similar to that of direct-gap GaN and ZnO [Phys. Rev. Lett. 113, 085501 (2014)]. Doping wide-band-gap (WBG) materials is among the most difficult challenges, with p-type GaN perhaps the only exception. As a promising low-cost alternative, ZnO has attracted significant attention. However, stable p-type ZnO is still a major obstacle, due to the formation of small polarons. A new type of polaron explains why GaN can be p-doped with Mg, whereas ZnO cannot be p-doped with Li. The unique feature of the polaron in GaN lies in its highly anisotropic localization. In contrast, the same polaron in ZnO cannot sustain such an anisotropic localization: a spontaneous symmetry breaking leads to a deep hole state [Phys. Rev. B 90, 165301 (2014)].

Electronic Structure and Fundamental Physics of Semiconductor Nanostructures

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Funding: \$210,000 (2014)

PROGRAM SCOPE

Project scope: Testing our fundamental understanding of the basic interactions that govern the electronic properties of semiconductor nanostructures requires access to spectroscopically rich and highly resolved data. Alas, this is afforded mostly by rather large nanostructures such as self-assembled epitaxial systems (InAs/GaAs; HgTe/CdTe; GaAs/AlAs), containing typically 100,000 or 1,000,000 atoms per computational unit cell. This size regime is well outside the range of DFT methodologies. At the same time, continuum-like methods (based on envelope functions) that can handle large nanostructures lack the atomistic resolution needed to describe the underlying electronic structure phenomenology. Using our previously developed screened-pseudopotential plus configuration interaction approach we can directly address million-atom nanostructures of the sort described above. Our scope is to use this methodology for understanding fundamental electronic processes in nano and eventually meso-scopic systems

FY 2014 HIGHLIGHTS

Highlights: The way large scale calculations lead to theoretical discovery of new nanostructure mechanisms (i) Discovery of a first-order, giant Rashba spin splitting in semiconductor nano wires; (ii) the discovery of a novel channel of light-hole to heavy-hole coupling in strained quantum dots, mediated by intermediate states (analogous to super exchange in magnetism), (iii) prediction of emergent density of states features in nanowires that are not associated with the conventional, orbitally classified states such a 1S, 1P, 1D. (iv) Microscopic explanation of the spectroscopic features observed in million-atom quantum dots embedded in nanowires. (v) Careful calculation of the electronic states in HgTe/CdTe quantum wells at the critical well thickness where topological band inversion occur shows that the relevant HH1 and E1 states anti-cross rather than cross, leading to gapped Dirac cones.

Unconventional Spin and Orbital Ordering in Semiconductor Nanostructures

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Funding: \$140,000 (2014)

PROGRAM SCOPE

Semiconductor nanostructures, such as quantum dots (QDs), provide an interesting interplay of interaction effects in confined geometries and novel opportunities to control the spin and orbital ordering at the nanoscale. However, owing to the computational complexity of including even a small number of magnetic impurities (~ 10), there is a need to apply various approximations schemes to accurately describe magnetic QDs. Unfortunately, a widely used mean-field theory leads to spurious phase transitions and an incorrect description of a carrier density in small magnetic systems. These difficulties impede the progress in understanding of the fundamental properties and the potential applications of semiconductor nanostructures. To systematically address this situation, our main objectives are: (i) developing a comprehensive framework suitable to study the interplay of many-body effects and quantum confinement in small magnetic systems, focusing on the inclusion of spin

fluctuations and developing computational methods beyond the mean-field approximation. (ii) exploring novel possibilities for the control of spin and orbital ordering in semiconductor nanostructures, as well as to provide proposals for their experimental implementation.

FY 2014 HIGHLIGHTS

The ground state of a nonmagnetic quantum mechanical system is widely expected to be nodeless. While this notion also provides a valuable guidance in understanding the ordering of energy levels in semiconductor nanostructures, there are reports that nodal ground states for holes are possible. However, the existence of such nodal states has been debated and even viewed merely as a theoretical artifact. We reveal [Phys. Rev. B 89, 045315 (2014)] that nodal ground states in quantum dots are not limited to a specific approach. Remarkably, the emergence of nodal hole states at the top of the valence band can be attributed to the formation of orbital vortex textures through competition between the hole kinetic energy and the coupling to the conduction band states. A novel magnetic semiconductor (Ba,K)(Zn,Mn)₂As₂, isostructural to 122 Fe-based superconductors, has a decoupled spin and charge doping, unlike the vast majority of magnetic semiconductors. This provides a unique opportunity to elucidate the microscopic origin of the magnetic interaction and ordering in dilute magnetic semiconductors (DMS). We show that [Phys. Rev. B 90, 140403(R) (2014)]: (i) the conventional density functional theory accurately describes this material, and (ii) the magnetic interaction emerges from the competition of the short-range superexchange and the longer-range spin-spin interaction mediated by the itinerant As holes. We predict a clear path to enhance Curie temperature, T_C , in novel DMS with an already record-high T_C . Realizing acoustic analogues of active optical devices has been a long-standing challenge. Phonon lasers could provide versatile sources of coherent acoustic waves used 3D imaging of nanostructures or creating periodic strain of a material to rapidly modulate its optical and electronic properties. We propose a nanoscale realization of a phonon laser utilizing phonon-assisted spin flips in quantum dots to amplify sound [Phys. Rev. Lett. 111, 186601 (2013)].

DOE National Laboratories

Integrated Modeling of Novel Materials

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Funding: \$541,195 (2014)

PROGRAM SCOPE

Complex electronic materials exhibit strong electronic correlations along with strong electronic coupling to multiple degrees of freedom, like lattice and spin. New data reveal substantial spatial inhomogeneity in superconductors, heavy fermion materials and at interfaces. This project follows two new directions: investigation of the role of interfacial interactions and competing states that emerge in films and properties of materials with Dirac spectrum of excitations. Theoretical understanding of the role of inhomogeneity, coupling to spin and lattice degrees of freedom and competition is a crucial missing step in our understanding of complex materials. The overarching goal of the project is to provide an

understanding of the fundamental physical processes that are important in determining the nanoscale inhomogeneity and coupling to other degrees of freedom in correlated electronic materials. Physical processes include: drivers and mechanisms of inhomogeneity, coupling to local lattice and spin degrees of freedom, transport and dynamics. Our goals are to discover new laws that govern the behavior of states of matter and to create the essential new understanding demanded by these discoveries. The hypothesis of our research approach is that correlations and competing interactions are manifested in both real and momentum space inhomogeneity, as seen in STM (scanning tunneling microscopy), NMR (nuclear magnetic resonance), and ARPES (angle resolved photo emission spectroscopy) data. Therefore, we are developing theoretical models and computational tools that focus on competing states due to momentum space anisotropies and spatial inhomogeneity. Our approach will allow for combined techniques that make contact with a momentum space characterization of inhomogeneous materials.

FY 2014 HIGHLIGHTS

1) We continue developing many-body methods combined with density functional theory to investigate the consequences for electron mass renormalization, electronic hot spots in the spectral function, and stability of superconductivity against competing states. 2) We are developing a parallel lattice BdG (Bogoliubov-de Gennes) code for studying the response functions in superconductors with spatial inhomogeneities and momentum space anisotropies in the bulk and at interfaces. An existing BdG code has been developed for multiband materials like the pnictide superconductors. We further develop algorithms for model calculations relevant to the pnictide and heavy-fermion superconductors and topological materials. 3) We developed understanding between the interplay of electronic correlations and electron-phonon coupling in correlated electron systems by solving the Anderson lattice model within the Gutzwiller approximation. 4) Inelastic Electron Tunneling Spectroscopy and negative U superconductivity in Dirac Materials. We have developed a formalism to investigate inelastic electron tunneling spectroscopy in topological insulators and in graphene. Inelastic scattering leads to the formation of negative U centers that can serve as nucleation centers for superconductivity on the surface of topological insulators and graphene.

EARLY CAREER: First Principles Predictions of Phase Stability in Complex Oxides

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Funding: \$400,000 (2014)

PROGRAM SCOPE

The goal of this project is to use first principles methods to predict materials with enhanced properties that can be synthesized and remain active under device relevant conditions. This project aims to develop and implement robust, high-throughput computational approaches for exploring phase stability. The ultimate goal is to facilitate the prediction-to-synthesis process through a synergistic effort involving (i) electronic structure calculations for properties predictions, (ii) phenomenological/empirical models for examining phase stability and (iii) experimental validation. The abundance of possible cation chemical identities and arrangements makes complex oxides (such as perovskites) an ideal playground for first principles studies. This variability gives rise to an array of physical, chemical, electrical and

magnetic properties as well as possible competing structures. First year efforts have emphasized properties predictions; primarily in ferroelectric/piezoelectric oxides and oxide interfaces and surfaces.

FY 2014 HIGHLIGHTS

(1) Modelling disorder in perovskite solid solutions [Voas *et al.*, *Phy. Rev. B* 90, 024105 (2014)]: Disorder in relatively ordered $K_{0.5}Na_{0.5}NbO_3$ supercells (a promising lead free piezoelectric) was modeled employing the special quasirandom structure method. Using this method we showed that the transition between the high temperature Pm and low temperature R3c phases is driven by Na-O interactions. As such, this method could be useful for discovering new high-response piezoelectrics. (2) Transparent conducting oxides: A delta-doped approach [Cooper *et al.*, *Sci. Rep.* 4, 6021 (2014)]: In a joint theory and experimental study, a new class of transparent three-dimensional conducting oxides was discovered based on the control of spacer layer thickness in 2D conducting oxide heterostructures. This transparent conducting oxide has transparency and electron mobilities similar to that of the more expensive indium-tin-oxide (ITO) and thus may be a useful alternative transparent electrode. (3) Polar catastrophe at the $SrTiO_3$ (111) surface [Sivadas *et al.*, *Phy. Rev. B* 89, 075303 (2014)]: Using density functional theory, we investigated the surface electronic structure of $SrTiO_3$ (111) slabs. We find that it is possible to create a 2d electron gas at these surfaces. The observed thickness dependent carrier densities, emphasize the importance of understanding the competition between electronic reconstruction and polar distortions when analyzing the 2D electron gas (2DEG) behavior of (111) and (110) interfaces. (4) Antisite defects in a pristine cathode material [H. Dixit *et al.* *ACS Nano*, DOI:10.1021/nn505740v (2014)]: Using atomic-scale theory and experiment we identify Ni antisite defects as the predominant defects in pristine (uncycled) lithium-manganese-rich oxide cathode material. Furthermore, these defects have facet-dependent formation energies. These results suggest that by controlling electrode surface orientation defect behavior can be altered, thus having implications for improving battery performance.

Theoretical Studies of Collective Phenomena

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Funding: \$1,301,000 (2014)

PROGRAM SCOPE

This project studies the emergence of complex collective electronic states in several families of materials, and their possible competition, or cooperation, in special regimes of temperatures, carrier densities, and external fields. The specific materials that are being investigated by our team include pnictides and cuprates high critical temperature superconductors, ferrites, cobaltites, molecule-based magnets, multiferroics, and a variety of artificially-created superlattices and interfaces involving oxide perovskites. These compounds are characterized by having several simultaneously active spin, charge, and orbital degrees of freedom, forming complex states where the many competing tendencies are delicately balanced. Our overarching goal is to reach a sufficient degree of understanding and control of model Hamiltonians for broad classes of materials with competing tendencies such that quantitative

predictions can be achieved. Our most recent work have addressed three specific objectives: (1) study of new collective states that may appear in artificial heterostructures, with associated exotic transport properties; (2) study of competing interactions in frustrated magnets and associated multiferroic tendencies; (3) study of the Fe-based superconductors in the intermediate on-site Coulomb repulsion regime via spin-fermion models and search for novel states with spin and orbital order. All these challenging topics are at the frontier of research in Condensed Matter and Materials Science. Ours is a synergistic team that takes advantage of the ORNL research environment via several collaborations with other BES-supported experimental and theoretical teams, as well as with researchers at the local neutron and computational user facilities.

FY 2014 HIGHLIGHTS

We have used microscopic models to predict the orientation dependence of the critical magnetic field for BiFeO₃. The model we developed is now being employed to describe the directional dichroism of BiFeO₃, or the change in optical absorption when the direction of propagation of light or, equivalently, the direction of the magnetic field, is reversed. *Ab initio* calculations of BiFeO₃ have shown that the polarization induced by the magnetic order below T-N actually points opposite to the ferroelectric moment above T-N, in agreement with recent measurements. Dynamical mean field theory (DMFT) calculations were performed for Co oxides and artificial heterostructures of Au- and Ir-based oxides. These calculations revealed that Co oxides undergo a transition from a mixture of high-spin and low-spin states to a purely low-spin state by reducing the dimensionality from 3D to 2D. This accounts for experimental results of optical and x-ray spectroscopy. Based on tight-binding modeling and density functional theory calculations, this FWP predicted that artificial heterostructures of Au- and Ir-based oxides grown along the [111] crystallographic axis would become novel topological insulators (TIs). DMFT calculations taking into account strong correlation effects confirmed the TI state in the Au-based oxide heterostructure.

SciDAC: Optimizing Superconductor Transport Properties through Large-Scale Simulation

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Funding: \$514,000 (2014)

PROGRAM SCOPE

The SciDAC partnership 'Optimizing Superconductor Transport Properties through Large-Scale Simulation' (short: OSCon) was established in September 2012. The main objective of this project is to develop and apply novel methods for optimizing superconductors for energy applications using large-scale computational algorithms and tools. The resulting numerical tools will pave the way for a systematic method to design superconductors with high critical currents. So far the quest for optimal superconductors with respect to largest critical current was only conducted via the Edisonian process of laborious experimental trial and error. OSCon is a joint effort of the Materials Science Division (MSD) and the Mathematics and Computer Science Division (MCS) of Argonne National Laboratory. The overall

project is carried out in collaboration with SciDAC Institutes using large-scale computation and leveraging DOE's leadership-class computing facilities.

FY 2014 HIGHLIGHTS

List of FY 2014 Highlights : (1) Iterative GPU solver for the large λ -limit completed, supplemented with highly flexible and sophisticated pinning landscape generator: Details, performance tests, and examples are written up and submitted to the Journal of Computation Physics; Detailed study of the weighted Jacobi method to optimize the performance concluded. (2) First critical current optimization results: In collaboration with the SciDAC institutes FASTMath and SUPER PIs we conducted several case studies of pinning configuration with small number of optimization parameters showing very encouraging results; two papers on optimal random arrays and regular square arrays are being prepared at present. (3) Scalable unstructured mesh code stabilized and in the process of being deployed on leadership class computers (Mira) (4) Advanced vortex detection and tracking: In collaboration with the SciDAC Institute SDAV (PIs Tom Peterka and Carolyn Phillips) we developed advanced vortex detection and tracking algorithms, which help to analyze and understand the underlying dynamical processes in superconductors (two papers submitted). Postdoc Hanqi Guo was hired in FY 2014 to do data analysis and visualization. (5) Successful explanation of dynamics in superfluids: In collaboration with the group of Kathy Levin we studied defect dynamics in superfluids; ASCR highlight submitted (6) Several experimental verifications (papers submitted or in preparation): Understanding the effect of competing defects (columnar and nanorods). Simulations explain experimental results quantitatively; Reentrance of superconductivity in parallel fields explained; Direct simulation of exact nano-particle pinning landscape observed in experiments – simulation shows almost perfect agreement; Vortex crossing and tilted field dynamics in experiment explained through simulations; Simulations of BZO nanoparticles plus strain field defect simulated. (7) Received time allocation on the Mira/Tukey supercomputer.

Network for *Ab Initio* Many-Body Methods: Development, Education and Training

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Students:	1 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	\$882,000 (2014)

PROGRAM SCOPE

For many classes of materials and molecular systems we lack predictive computational quantum mechanical methods, where the properties and performance can be reliably calculated to high accuracy without empirical tuning of parameters. This project focuses on the continuum quantum Monte Carlo (QMC) method, which offers a path towards these high accuracy calculations for a broad range of electronic systems and is potentially systematically convergeable to give exact results. Localization, van der Waals interactions, and strong electronic correlations can all be treated with high fidelity. These are areas where established electronic structure methods have great difficulty. The importance of a

predictive capability cannot be overstated: it is the very foundation of viable efforts in computational materials design. The proposed research brings developers of electronic structure methods together to build a QMC framework supporting continuing theoretical development, broader scientific application, and use in changing computing environments. The outcome of this collaboration – advanced software, efficient workflows, and data repositories – will increase productivity and fundamentally alter how QMC data are produced, acquired, processed, and used by the materials and chemistry community at large. The next-generation QMC methods and software will first be applied to catalysis, defects, high-pressure materials and establish benchmark materials problems. Our work will provide direct answers to fundamental materials science questions in these areas and establish benchmark levels of accuracy that will, in turn, provide insight and targets for future developments in other electronic structure approaches.

FY 2014 HIGHLIGHTS

In FY 2014 we published an Editors' choice article, Shulenburger & Mattsson Phys. Rev. B (2013), carefully benchmarking QMC calculations for solids. The test set of solids included ionic, metallic, covalent, and van der Waals bonded materials. This article is the first to comprehensively and systematically determine the accuracy of the standard QMC approach, via careful extrapolation and convergence testing of all quantities. These calculations only became possible due to advances in DOE computational platforms and large allocations, e.g. through the INCITE program. The insights into the method help guide the future activities of this project and guide others on the practical accuracy of the current approach. We continued to perform benchmark calculations including (i) a study of the performance of different density functionals for bulk water using QMC, (ii) a study of van der Waals interaction dominated systems, ranging from noble gas solids to DNA, and (iii) high pressure hydrogen. Overall in FY 2014 we published 8 articles including two Physical Review Editors' choice. David Ceperley gave an invited talk on the project at the American Physical Society March Meeting. As part of our goal of improving accessibility of Quantum Monte Carlo (QMC) methods, in FY 2014 we made several public releases of the open source QMCPACK code, and developed and a new QMCPACK website, <http://www.qmcpack.org> . The new releases include automation tools that significantly enhance productivity for new and expert users. We organized a training workshop, held 14-18 July at Argonne Leadership Computing Facility, with 33 trainees including 1 from industry. The workshop covered fundamental aspects of QMC through to practical calculations for molecular and solid-state systems. Every member of the project was onsite for the full week to assist with training, labs, and developing new QMCPACK users. The training sessions were recorded and are published at the video sharing website YouTube.

Electronic Properties of Transition Metal Compound Nanotubes

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Funding: \$296,000 (2014)

PROGRAM SCOPE

The goal of the program is to study nanoscale physics in transitional metal compounds and in the nanotubes. The program employs density functional theory and the Wannier function toolset developed in the program, supplemented by low-energy effective model suggested by these studies for a better illustration of underlying physics. Recently, we have been focusing on three main directions: 1) effects of glide translational symmetry in Fe-based superconductors, 2) signatures of topological quantum phase transition in insulators 3) propagation and decay of local excitations, and 4) systems with simultaneously strong spin-orbit coupling and electronic interactions (e.g. the irridates). In addition to the studies of physical effects in real materials, the program also includes an important effort of developing new theoretical/numerical method to address new territories of problems not possible with current technology. A good example is our recent development of an *ab initio* Wannier function method to incorporate disordered impurities in full, a task previously impossible to achieve without dropping the essential multiple scattering processes between impurities.

FY 2014 HIGHLIGHTS

1. Develop a new method to study propagation and decay of local excitations in materials, and predicted excitonic band structures later verified by X-ray experiment. 2. Investigate various spectroscopic signatures of quantum topological phase transition in insulators. 3. Investigate the effects in electronic structure and pairing symmetry of the glide translational symmetry. 4. Study pseudogap and degeneracy lifting with fluctuating ferro-orbital order in Fe-based superconductors.

Dynamical Mean Field Theory for Oxide Heterostructures

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Funding: \$299,000 (2014)

PROGRAM SCOPE

The use of advanced methods for strongly correlated materials has traditionally been confined to simplified models with few parameters, and without a systematic connection to the underlying electronic structure. This glue grant aims to exploit dynamical mean field theory in a realistic context, by developing techniques for rapid solution of the many body kernel, and by connecting *ab initio* electronic structure to simplified models in a realistic and transferable way. As a linked project (following on from seed funding), we have developed models for collective phenomena in multiferroic oxides, focusing on control of structure and thermodynamic properties.

FY 2014 HIGHLIGHTS

- We have successfully used machine learning methods to replace the auxiliary solver at the heart of Dynamical Mean Field Theory (DMFT), which is the most computationally intensive part. This will aid high throughput electronic structure calculations of correlated materials.
- We are porting DMFT codes onto Argonne's Leadership Computing Facility.
- We have used related methods to explore the potential

role of oxygen defects as the progenitors of magnetism in SrTiO₃ in combination with electrostatic doping. • We have generated a new model for the electrocaloric effect, explaining why it is in general small, and offering a path to develop materials where it is enhanced.

Theory of Materials Program

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Funding: \$735,000 (2014)

PROGRAM SCOPE

The goal of this program is to understand and compute material properties and behaviors, covering a range of systems that include complex materials, surfaces and interfaces, nanostructures, superconductors, and strongly correlated electron systems. Novel materials and new concepts are explored. A variety of theoretical techniques is employed, ranging from first-principles electronic structure methods and many-body perturbation theory approaches to new conceptual and computational frameworks suitable for complex materials/nanostructures and strongly interacting systems. One emphasis is to investigate realistic systems employing microscopic first-principles approaches, including many-electron effects. Model systems are also examined. Close collaboration with experimentalists is maintained. Another emphasis is to push theory beyond the Landau paradigm toward a framework suitable for very strongly correlated systems. New phenomena, new phases, and new organization principles may be discovered. Equally important is the development of computational methods suitable for increasingly complex materials and strongly correlated materials.

FY 2014 HIGHLIGHTS

This program has made a number of advances in understanding reduced dimensional systems, topological phases, superconductivity, nanostructures, molecular interfaces, as well as in theory and method development. We obtained an explicit formula for optical oscillator strength of excitons in carbon nanotubes (CNTs) and developed a theory of multiple exciton ionization in shallow doped CNTs. For 2D systems, we predicted novel and diversity of excitons in monolayer transition metal dichalcogenides that were subsequently confirmed by experiment, provided first-principles calculations of satellite structures in the spectral function of 2D electron gas systems, analyzed the effects of charge doping and constrained magnetization on the electronic properties of monolayer FeSe, and predicted the effects of doping on excitons and quasiparticle lifetimes in graphene. We moreover discovered the novel phenomenon of electron supercollimation in graphene and other 2D Dirac fermion systems using 1D disorder potentials. We showed the microscopic coexistence of spin density wave and superconductivity in underdoped NaFe_{1-x}Co_xAs and developed a general approach to calculate shallow defect levels in semiconductors. We demonstrated critical theories of phase transition between symmetry protected topological states and gapped symmetric edges of such states. We predicted theoretically and subsequently demonstrated experimentally that the spin polarization of

photoelectrons from topological insulators may be tuned and controlled using the polarization of the incident light. We performed nonadiabatic molecular dynamics simulation for hole transport in organic molecule monolayer, explained the highest rectification ratios measured in molecular devices, and obtained a hybrid functional for polarization-induced gap renormalization in molecular solids.

Condensed Matter Theory

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Funding: \$1,520,000 (2014)

PROGRAM SCOPE

Condensed matter theory research programs are carried out in the areas of superconductivity, magnetism, and low dimensional systems, with an emphasis on interaction with other programs at Argonne. Our long term goal is to make fundamental advances in condensed matter physics as it relates to BES mission goals. In particular, we desire to make a major impact in a number of important endeavors, including the understanding of high temperature cuprate and pnictide superconductors, other transition metal compounds with novel properties such as quantum spin liquids and charge density waves, topological properties of metallic and nanostructured magnets, quantum phase transitions in strongly correlated electron systems, and transport in quantum wires, quantum dots, and spintronic devices. We are also developing as a center for theoretical analysis of spectroscopic and imaging data, not only within the context of MSD programs, but also those at the Advanced Photon Source and Argonne's Center for Nanoscale Materials, as well as other DOE national lab programs.

FY 2014 HIGHLIGHTS

- Showed that the magnon spectrum in magnetic thin films can be manipulated through periodic topographic modifications of the thin film.
- Demonstrated that the reversal mechanism in spin-torque random access memories becomes dominated by ferromagnetic exchange for sizes 50 nm and smaller.
- Demonstrated that superconductivity smears the Lifshitz topological transition as a consequence of particle-hole mixing.
- Investigated multiband superconductors in a magnetic field and demonstrated that fluctuations are enhanced at the magnetic field scale set by the band with the largest coherence length.
- Developed a systematic approach to calculate energies of periodic and quasiperiodic arrangements of interacting particles.
- Discovered exotic collective nematic Wigner crystal and supersolid phases of bosons in frustrated 2D lattices.
- Showed that the true low-energy excitations in one-dimensional quantum liquids have fermionic statistics, regardless of the statistics of the constituent particles.
- Developed a theory of equilibration of strongly interacting electrons in quantum wires and established the crucial role played by the coupling of spins of next-nearest neighbor electrons.
- Found that cuprates are on the border between uniaxial and biaxial charge order by a Ginzburg-Landau analysis with coefficients derived from photoemission data.
- Demonstrated that inelastic neutron scattering

data on the spin liquid material Herbersmithite are consistent with antiferromagnetic coupling between copper spins on neighboring Kagome planes.

Materials Project for Functional Electronic Materials Design

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Daniel Gunter; Lawrence Berkeley National Laboratory
Maciej Haranczyk; Lawrence Berkeley National Laboratory
Mark Asta; Lawrence Berkeley National Laboratory
Shyue Ping Ong; California-San Diego, University of
Jeff Snyder; California Institute of Technology
Students: 9 Postdoctoral Fellow(s), 4 Graduate(s), 0 Undergraduate(s)
Funding: \$500,000 (2014)

PROGRAM SCOPE

The Materials Project aims to accelerate materials discovery and education through advanced scientific computing and innovative design methods, scale those computations to cover all known inorganic compounds, and disseminate that information and design tools to the larger materials community. Specifically the Project will achieve this by: • Providing unprecedented data and materials design tools as well as comprehensive capabilities for scientists to share their processes and results. • Leveraging high-throughput calculations, state-of-the-art electronic structure methods as well as novel data mining algorithms for surface, defect, electronic and finite temperature property predictions for tens of thousands of materials to yield an unparalleled materials design environment. • Demonstrating the derived data and infrastructure in the design of novel functional electronic materials: photovoltaics, thermoelectrics, transparent conductors and photocatalytic materials.

FY 2014 HIGHLIGHTS

The Materials Project (www.materialsproject.org) – part of the broader Materials Genome Initiative - is an effort to compute the properties of all known inorganic materials and beyond, and offer that data to the community together with online analysis and design algorithms. The current release contains data derived from density functional theory (DFT) calculations for over 54,000 materials, each with searchable associated properties such as relaxed structure, electronic state, energy storage capability, aqueous and solid stability, and more. Furthermore, software algorithms are offered by the Materials Project and can be used by researchers for materials informatics, including both interactive web-based tools like the Phase Diagram App and the Pourbaix App, as well as open-source codebases and data access tools such as the pymatgen materials analysis library, FireWorks workflow software, and Materials API (www.github.com/materialsproject). The MP Pourbaix App operates through an in-house developed reference scheme and constitutes – by orders of magnitude - the largest available resource for solid-aqueous phase stability, comprising > 70,000 Pourbaix diagrams. Showcasing the capabilities of

the Materials Project, the team has successfully explained why the CaCO_3 polymorph aragonite is formed rather than the stable calcite under modern seawater conditions – a fact that has tremendous implications for biomineralization, paleogeochemistry, and the vulnerability of marine life to ocean acidification. The suite of easily available online data, algorithms and open-source codes has attracted 8,500 registered users with – on average – > 40,000 page, > 6,800 sessions, and > 3,000 unique visitors per month. This combined data strongly indicates that the Project is being heavily used and is becoming a unique resource in the materials science community.

Extending the Reach of Computational-Theoretical Methods to Materials at the Energy Frontier

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Funding: \$1,327,000 (2014)

PROGRAM SCOPE

This program is designed to overcome materials theory challenges that are both at the frontier of basic research and beyond current theoretical and computational capabilities. Our overarching goal is to significantly improve our description and understanding of electronic correlations and magnetic interactions in an *ab initio* framework. A new effort is under way, focused in highly correlated materials and magnetic oxides. The first QMC results of defects in correlated oxides are currently under peer review. Our goal is to describe the physical, chemical, and electronic properties of magnetic and highly correlated materials with accuracy comparable to experimental characterization and in large, physically-relevant systems. This program includes both accurate *ab initio* approaches and methods development based on simpler systems or models. Models will allow us to test and develop new approaches which can be next extended to real materials. A priority is to develop, improve, and implement new theories that go well beyond the current approaches to exploit high-performance computers (HPC). We thus focus on stochastic methods such as quantum Monte Carlo (QMC) or the Wang and Landau (WL) free-energy method because of both accuracy and scalability in HPC. Many relevant properties of semiconductors, polymers, correlated, oxides, and magnets are currently beyond the accuracy obtainable with the state-of-the-art approaches based on Density Functional Theory (DFT). Accordingly, we aim to provide an alternative route using the highly accurate QMC and/or improve DFT approximations (e.g. for finite temperature) with WL. In the short term, the results provided by our research will quantify the errors of the state of the art approximations of DFT that are widely used. In addition, we aim to provide an alternative stochastic-based approach to reach the required accuracy for energy applications.

FY 2014 HIGHLIGHTS

We have generated a set of pseudopotentials for light transition metal elements Sc to Zn to be used in QMC calculations for transition-metal oxides. We found that QMC calculations require including semi-core electrons in the valence. Our pseudopotentials are moderately hard, requiring a planewave cutoff

energy of about 500 Ry and a small nonlocal cutoff radius. However, the pseudopotentials can be softened to around 300 Ry using an optimized approach without greatly impacting the overall level of accuracy. A lower energy cutoff results in significant memory savings, which in turn permits the study of larger systems with more electrons such as bulk transition metal oxides and even point defect systems with modest supercells. These pseudopotentials have allowed the calculation of magnetic coupling constants in cuprates and defect formation energies in ZnO. Calculations of other binary and ternary oxides are in progress. We derived a general scheme to calculate the magnetic exchange interaction, local anisotropy and anisotropic exchange due to spin-orbit coupling in metal and alloys. We have expanded our statistical description of magnetic systems (WL-LSMS) to include longitudinal fluctuations of the magnetic moments going beyond a rigid spin Heisenberg model (e.g. Ni). We have investigated the convergence behavior of the parallel replica exchange and implemented this algorithm on massively parallel architectures. We have developed an *ab initio* based “Enthalpy Matrix” that correctly identifies all known single-phase high-entropy alloys (HEAs) while rejecting similar elemental combinations that do not form a HEA. We have made predictions of new 5-, 6-, and 7- elemental HEAs. The absolute convergence of Full-Potential Multiple Scattering Theory electronic structure methods in terms of the underlying angular momentum expansion parameters has been demonstrated and implemented in the linear scaling LSMS method for treating large cell models complex materials.

Discontinuous Methods for Massively Parallel QMD: Li-ion Interface Dynamics from First Principles

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Funding: \$361,000 (2014)

Jointly funded by the Chemical Sciences, Geosciences, & Biosciences Division and Materials Sciences and Engineering Division

PROGRAM SCOPE

We develop and employ for the first time new Discontinuous Galerkin (DG) and Pole Expansion/Selected Inversion (PEXSI) electronic structure methods to accomplish quantum molecular dynamics (QMD) on an unprecedented scale; and apply the new methodologies to address fundamental questions in energy storage: the formation and evolution of the solid-electrolyte interphase (SEI) layer in Lithium-ion cells. We employ state-of-the-art massively parallel planewave codes in the initial phase of the work while the new DG and PEXSI methodologies are developed and verified. We then apply the new methodologies to much larger systems, up to 10,000 atoms, in order to reach for the first time sufficient system complexity to effectively model complete liquid-on-anode configurations. The remarkable properties of the new methodology are made possible by releasing the constraint of continuity through the DG formulation of the Kohn-Sham equations. By virtue of these properties, our initial parallel

implementation has accomplished *ab initio* calculations with over 4,000 atoms with planewave accuracy. Initial DG QMD simulations show excellent energy conservation, with energy drift < 2 meV/atom/ps. To reach the largest system sizes, we develop and employ the new PEXSI methodology, eliminating the need for diagonalization while retaining strict systematic improvability and applicability to both metals and insulators. In partnership with the SciDAC FASTMath Institute, we have completed MPI parallelization of the PEXSI code, testing on a wide range of systems, documentation, and release (<http://www.pexsi.org>). The resulting code can scale to over 100,000 processors and has now been applied to systems containing over 45,000 atoms. Current work focuses on the combination of DG and PEXSI methodologies to reach the length and time scales necessary to model mixed-phase anode-electrolyte configurations to begin to understand for the first time the chemistry and dynamics at this critical interface.

FY 2014 HIGHLIGHTS

We accomplished all FY14 project milestones and commenced work on FY15 milestones. Four journal articles were published and five more submitted. We carried out an extensive series of QMD simulations of ethylene carbonate (EC), ethyl methyl carbonate (EMC), and EC/EMC mixture solvents with LiPF₆ salt, as widely used in practice. We found that Li prefers tetrahedral coordination in all electrolytes considered, consistent with experiment for EC, and providing a prediction for EMC and EC/EMC mixture. Most significantly, we found a key correlation of solvation and mobility in all electrolytes considered: the stronger the solvation, the less the mobility. This finding has the potential to significantly impact the engineering and improvement of Li-ion battery electrolytes going forward, and with that, battery systems as a whole. Regarding the new Discontinuous Galerkin (DG) computational methodology being developed to reach the needed length and time scales to model full anode-electrolyte systems, we made a number of advances. We implemented independent grids for density and wavefunctions, yielding accurate forces for all atomic species, soft and hard, metals and nonmetals alike. We implemented molecular dynamics, obtaining excellent energy conservation. We implemented MPI parallelization of local Kohn-Sham solves to form DG basis in each element, yielding a 70-fold speedup. Regarding the new Pole Expansion and Selected Inversion (PEXSI) methodology being developed to eliminate the need for diagonalization altogether, we parallelized, tested, documented, and released a full production code (<http://www.pexsi.org>). The new MPI code scales to over 100,000 CPUs. The new PEXSI code has been incorporated into the widely used SIESTA electronic structure code, yielding a factor of 18 speedup. Finally, we implemented the new PEXSI methodology with the DG basis to reach the largest length and time scales needed to model full anode-electrolyte configurations.

High-Performance First-Principles Molecular Dynamics for Predictive Theory and Modeling

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Funding:	\$165,000 (2014)

PROGRAM SCOPE

First-principles molecular dynamics (FPMD) simulations are used in a wide range of applications in chemistry, materials science and nanotechnology, and provide an accurate, atomic-scale model of matter based on a quantum mechanical description. We are working to develop a high-performance software infrastructure that combines large-scale FPMD simulations with on-the-fly computation of vibrational spectra and electronic excitations. The software includes a toolkit that enables the exploration of new statistical sampling methods. This research provides a powerful predictive simulation tool that enables the direct comparison of simulated data with experimental data such as infrared and Raman spectra, X-ray and neutron diffraction spectra as well as vibrational and optical properties measured at finite temperature or during chemical processes that involve breaking and formation of bonds. The software infrastructure is readily available to the general research community in an open-source format and will accelerate the process of discovery and optimization of new materials properties.

FY 2014 HIGHLIGHTS

Theoretical analysis of phase transition mechanisms using standard atomistic simulation methods is not feasible because such transitions involve rare barrier-crossing events with mean first passage time many orders of magnitude greater than the vibrational frequency of atoms. To overcome this time-scale issue we have implemented a free energy surface exploration tool in QBox. The method involves selecting a set of suitable collective variables (CVs), that can distinguish the different phases in super cooled water, and the information required to evolve these CVs is extracted by evolving the underlying atomic system. The method involves an adiabatic time-scale separation between the electrons and the ions and also between the atomic vibrational motion and the evolution of the CVs. The replica-exchange molecular dynamics (REMD) approach has been successfully implemented within the Qbox client-server model. REMD allows exploration of the whole configuration space by running multiple trajectories at different temperatures to accelerate the sampling. The resulting trajectories contain a wealth of information that can be fed to dimension reduction techniques like diffusion maps, principle component analysis, etc. to identify the dimensions of the slow manifold involved in a phase transition. Our initial analysis of the liquid-liquid transition in water, using PBE exchange correlation functional, suggests that we need at least three order parameters to understand microscopic mechanisms associated with the proposed liquid-liquid transition in super cooled water.

Materials Theory

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Students: 3 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding: \$1,322,000 (2014)

PROGRAM SCOPE

This project uses state-of-the-art materials specific theoretical tools to develop understanding of materials. Working in conjunction with ORNL and external experimental efforts, we unravel the chemical and structural underpinnings of collective properties in specific materials, develop understanding of novel phenomena and materials, and devise new compounds with useful properties. The essential aspect is the use of methods that directly incorporate the chemical make-up and detailed structure of materials and so enable direct connections with experiments. Impacts of this work include microscopic understanding of materials properties with emphasis on functional materials. Our effort includes materials with exceptional (low or high) thermal conductivity, correlated magnetic materials, transparent conductors, intercalation compounds for energy storage, superconductors, and materials with unusual characteristics, such as uncommon bonding patterns. Questions that we will address are: How do interesting and useful properties arise? How can we modify materials to achieve and control properties and function? What are the chemical and structural motifs that lead to interesting and useful properties? In what materials should we expect the unexpected (i.e. where are there intense competitions between ground states that may lead to novel behavior)? The overarching goal behind this is materials discovery.

FY 2014 HIGHLIGHTS

- Predicted two new chalcogenide semiconductors, one of which is a candidate p-type transparent conductor. These were subsequently synthesized experimentally at ORNL and shown to have the predicted properties. This provides a rare example of a new bulk functional material predicted theoretically and subsequently confirmed experimentally.
- Showed that the Fe-based compound YFe_2Ge_2 is near a magnetic quantum critical point with features closely related to the Fe-pnictide superconductors, although it does not contain pnictogens or chalcogens.
- We found an extremely inhomogeneous, fractal like electronic structure and lattice distortion in metallic IrTe_2 arising from frustration of Te p-electron bonding.
- Discovered that the transparent conducting oxide BaSnO_3 has exceptional tunability in its optical properties via volumetric strain and that interfacial two dimensional electron gasses based on stannate and transition metal perovskites interfaces may be achievable.
- Identified two new silicide magnetic semiconductors.
- Found that Ta_2PdS_5 and $\text{Ta}_4\text{Pd}_3\text{Te}_{16}$ are multiband superconductors explaining the very high upper critical field and other anomalous properties.
- Refined density functionals for van der Waals interacting materials and identified strategies for further improving this class of functional.
- Calculated the thickness depend surface carrier concentration on 111 terminated SrTiO_3 .

Condensed Matter Theory

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Wei Ku; Brookhaven National Laboratory
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Funding: \$1,406,000 (2014)

PROGRAM SCOPE

The goal of the program is to study systems with strong correlations and systems out of equilibrium. Such studies provide us not just with important new insights into fundamentals of condensed matter physics, but also have practical importance for discovery and development of new materials. Strong correlations emerge either as a result of strong lattice interactions or, in low dimensional systems, due to strong quantum fluctuations. Examples of such systems include Mott insulators, quantum magnets, systems close to quantum criticality, heavy fermion materials and many others. Strong correlations playing especially prominent role in out-of-equilibrium make the traditional computational methods ineffective. Our group has developed new ones based on a combination of methods of integrable field theory and numerical methods.

FY 2014 HIGHLIGHTS

(1) In collaboration with Prof. A. Chubukov (Wisconsin) we developed a theoretical description of the phase transition in the cuprates separating the pseudo gap region from the rest of the phase diagram [Phys. Rev. B 89, 184515 (2014)]. (2) In collaboration with Prof. M. Aronson's group at BNL we studied Quantum Critical Point in the non-Fermi liquid metal YFe_2Al_{10} [Proc. Nat. Academy of Sciences. pnas.1413112111.]

Materials Theory Institute

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Sr. Investigator(s):
Students: 0 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding: \$238,000 (2014)

PROGRAM SCOPE

Materials Theory Institute (MTI) aims to attract world-leading theorists for visits of one week to six months to broaden the base and the scope of and bring new cutting-edge theory to the Materials Science Division (MSD). MTI selects topics and visitors in two categories: promising new opportunities arising from MSD research, and new directions in condensed matter and materials science arising from the broader community. MTI implements its goal through an intensive visiting programs, which bring top experts, both, distinguished scientists and outstanding young talents, to work on high impact problems and emerging topics and themes in materials theory and to bring new revolutionary science to MSD. The topics to be pursued and the respective visitors are selected by an internal Scientific Advisory Committee from competitive proposals solicited from all MSD staff and also from the outside researchers. MTI also identifies top early career and established theorists as candidates for recruitment to postdoctoral and permanent positions at Argonne. MTI holds topical workshops on the most urgent subjects related to existing MSD projects, which promise to stimulate new research directions at MSD.

FY 2014 HIGHLIGHTS

[1] We have studied the dynamical permittivity in ferroelectric film a few nanometer-thin carrying 180-degree periodic domain structure, sandwiched between two para-electric layers. The resulting

frequency-dependent permittivity demonstrates the sharp collective resonance mode at $\omega \sim 0.3 - 2$ THz. [2] Boltzmann's H-theorem stating that entropy of a physical system would tend to increase over time remains a foundation of thermodynamics. Original Boltzmann's formulation given for classical gases was resting on the molecular chaos hypothesis. Von Neumann's quantum H-theorem claimed quantum origin of irreversibility but included as a part of the proof macroscopic measurement procedure going thus beyond the strictly quantum consideration. Recent developments related entropy growth to quantum entanglement hinting the solely quantum origin of macroscopic irreversibility. In particular, progress in quantum informatics brought in several rigorous results on the conditions for the non-negative entropy gain. However, many questions of how to adapt them to the realm of physics remain. Utilizing the mathematical formalism, we show that entanglement of electrons with either electromagnetic environment or phonon bath results in the evolution of the electron density matrix that belong in the classes of evolution described in quantum informatics. Using exemplary physical systems we formulate and prove the H-theorem for a wide class of physical phenomena. [3] We studied the free-energy landscape of a minimal model for relaxor ferroelectrics. Using a variational method, which includes leading correlations beyond the mean-field approximation as well as disorder averaging at the level of a simple replica theory, we found metastable paraelectric states with a stability region that extends to zero temperature. The free energy of such states exhibits an essential singularity for weak compositional disorder pointing to their necessary occurrence.

Quantum Mesoscopic Materials and Structures

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Funding: \$741,000 (2014)

PROGRAM SCOPE

The goal of the Quantum Mesoscopic Materials Program is to explore the phenomena of quantum coherence and entanglement in order to develop predictive models and theories for the design of new materials with desirable properties and controllable behavior on the electron, atomic, and mesoscopic levels. Our strategy is based on creation of nanoscale metamaterials, such as granular structures, Josephson and hybrid arrays, and nanopatterned structures. At the initial stage we will focus on the exemplary superconductor-insulator transition that represents a unique coherent quantum phase transition. Building on the developed understanding of a superconductor-insulator transition as a manifestly quantum transition between the two quantum coherent superconducting and superinsulating states, we will perform an intensive theoretical analysis of quantum coherent effects in the vicinity of the superconductor-insulator transition (SIT), the role of the entanglement and related phenomena in formation irreversibility and glassiness in the finite quantum systems with the localized degrees of freedom. We define our strategic priorities as: 1. Comprehensive formulation of a theory of the superconductor-to-superinsulator transition emphasizing its quantum coherent nature, the role of Coulomb effects and quantum fluctuations. 2. Entanglement effects and their role in formation irreversibility and other macroscopic properties in inherently quantum systems. 3. Fluctuation effects both in the proximity of the superconductor-insulator transition and far from the transition both deep in the insulating and the superconducting states. 4. Quantum coherent transport utilizing the duality between the Aharonov-Bohm and Aharonov-Casher effects in disordered films, quantum wires and hybrid structures. 5. Fluctuation effects in conventional (type I and type II) and critical superconductors.

FY 2014 HIGHLIGHTS

(1) We investigated realization of the so-called Bogomolny critical regime, which was originally found in Abelian Higgs models at the border of type I-type II superconductivity in the finite weakly type II superconducting samples. The Bogomolny point at $\kappa_c=1/\sqrt{2}$ is characterized by infinite degeneracy of the superconducting state with respect to vortex spatial configurations. Finite-size system stabilizes normal domains and promotes their transient dynamics in the critical regime. We report that in mesoscale samples with dimensions commensurate with ξ , a vortex droplet, comprising a single normal domain, undergoes the Rayleigh instability at $\kappa \leq \kappa_c$ and decays by emitting a sequence of single vortices. We showed that at $\kappa \leq \kappa_c$ the repulsion mediated by the vortex stray fields prevails over the vortex core attraction and causes the fission of vortex droplets. We thus reveal Abrikosov-Nielsen-Olesen vortices of Abelian-Higgs models dynamics in finite systems with boundaries, which promises access to novel effects in quantum field theory via a bench-top laboratory experiment. (2) Understanding the resulting complexity of glassy behaviors is key to gaining insight into a variety of systems in nature, including spins and magnetic moments in magnetism, electrons in metals, Cooper pairs in disordered superconductors, vortices and interfaces in superconductors and magnets, social and neural networks, and protein folding, and remains one of the major challenges in physics. We developed an analytical approach based on the method of functional equations that allows us to construct Rayleigh approximation to the ground state of a two-dimensional (2D) random Coulomb system with logarithmic interactions. (3) We found a giant inverse proximity effect that arises in small low-dimensional superconductor-normal-superconductor (S/N/S) junctions, where the proximity coherence length is larger than the coherence length of a source superconductor.

Accelerated Molecular Dynamics Methods

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Funding: \$446,000 (2014)

PROGRAM SCOPE

Molecular dynamics (MD) simulation, a powerful tool for probing systems in full atomistic detail, is limited to a few microseconds or less, while many activated processes in materials take place on much longer time scales. Moreover, most real systems have a complexity that makes it difficult or impossible to accurately predict their dynamical evolution using intuition or simple models. Accelerated molecular dynamics methods, developed over the last 17 years at Los Alamos, offer a way out of this dilemma. Built on solid statistical mechanical concepts, these methods follow the long-time evolution of activated processes in full, accurate detail. Simulations so far on processes such as surface diffusion and growth, bulk diffusion, radiation damage annealing, and grain-boundary sliding and nanoscale kinetics provide insights that would have been virtually impossible to obtain by any other technique. We can reach time scales of ms, s, and beyond, and we invariably observe complex, unanticipated behavior, even in situations where the dynamics were expected to be simple. We are applying the methods to assist other DOE programs at LANL, and developing the methods further to overcome key obstacles, with the goal of making them applicable to the widest possible range of problems. In particular we are developing new

algorithms for treating more complex systems and making use of massive parallelism. We are also developing user-friendly software and collaborating on applications with experts from around the world. Feedback from the collaborations in turn shows us where further development is most needed.

FY 2014 HIGHLIGHTS

- Developed a method for computing exact rate constants that is efficient enough to use with density functional theory.
- Explained mechanism for crossover to anisotropic surface-directed growth of near-surface He bubbles in plasma-irradiated tungsten as growth rate is decreased to experimental rates.
- Developed a new way to achieve unprecedented efficiency from the parareal algorithm, which parallelizes time without requiring infrequent events.
- Developed a method for performing accelerated quantum dynamics, as appropriate for, e.g., hydrogen at or below room temperature.
- Provided a formal analysis of the accuracy of kinetics in coarse-grained molecular dynamics models for solids.

Exploratory Development of Theoretical Methods

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Sr. Investigator(s): Vladimir Antropov; Ames Laboratory
Viatches Dobrovitski; Ames Laboratory
Bruce Harmon; Ames Laboratory
Kai-Ming Ho; Ames Laboratory
Students: 2 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding: \$639,000 (2014)

PROGRAM SCOPE

The purpose of this FWP is to generate new theories, models, and algorithms that will be beneficial to the research programs at the Ames Laboratory and to the mission of DOE. This FWP will lead the development of theoretical tools to study a broad range of problems in physics, materials science, and chemical as well as biological systems. The generality of these tools allows the cross-fertilization of ideas from one problem to problems in an entirely different area through the common link of the mathematical formulation. Such leaps across topic areas and in some cases across disciplines are characteristic of the power of a fundamental physics-based approach to the development of new theoretical methods, facilitated by the availability of general theoretical tools applicable to very different sets of problems. Current efforts of this FWP includes (1) methods for accurate calculation of correlated electron systems; (2) methods for spin dynamics and quantum control of spin; and (3) methods for computational prediction and design of complex structures and materials.

FY 2014 HIGHLIGHTS

During FY 2014 we developed a LDA+Gutzwiller (LDA+G) method and computational code for studying correlated electron systems. The LDA+Gutzwiller method has been found to have accuracy similar to LDA+DMFT, yet performs thousands of times faster! The LDA+Gutzwiller method has been applied successfully to study the electronic structure of pnictide superconductors, iso-structural transformations in Ce, and energetics and electronic structure of Pu. The team developed a new first-principles density

functional theory based Gutzwiller wave function for correlated electron systems. A correlation matrix renormalization (CMR) method was also developed to treat two-particle interactions beyond the original Gutzwiller approximation. We developed theories for itinerant magnetism including strong spin fluctuation effects. Spin fluctuation effects in iron superconductors, 3d-metals Fe and Ni, and 5f-metal Pu, were investigated. We also developed novel theoretical techniques for investigating and controlling the quantum spin dynamics of the coupled individual electronic and nuclear spins in diamond, interacting with their solid-state environment and applied these tools to nanoscale sensing. Lastly, the team detailed an adaptive genetic algorithm method for crystal structure prediction. The method enables computational prediction of complex binary and ternary crystal structures as well as interface structures with unit cells as large as 50-200 atoms.

X-Ray Scattering

Institutions Receiving Grants

Resonant Soft X-Ray Scattering Studies of Spontaneous and Engineered Electronic Order in Transition Metal Oxides

Institution: Illinois-Urbana Champaign, University of
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Principal Investigator: Peter Abbamonte
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Students: 0 Postdoctoral Fellow(s), 3 Graduate(s), 1 Undergraduate(s)
Funding: \$252,796 (2012-2015)

PROGRAM SCOPE

The purpose of this project is to understand the interplay between engineered nanoscale order, created artificially by nanofabrication techniques, and the innate electronic instabilities in transition metal oxides. The term “instability” here refers to spontaneous electronic order such as stripe phases, charge or spin density waves, orbital order, or intrinsic electronic inhomogeneity due to proximity to a quantum critical point. The long-term goal is to understand how these two types of nanoscale order cooperate to create new phenomena, with hopes of contributing eventually to a revolution in strongly correlated electronic devices. This project is integrally tied to the development of new scattering techniques for the study of important phenomena in condensed matter. Progress with this project depends on access to materials that have been artificially structured with nanofabrication techniques. For this purpose, we have developed electron beam lithography techniques, using facilities in the Frederick Seitz Materials Research Laboratory, for fabricating very large arrays of transition metal oxide quantum wires. In addition, we have ongoing collaborations with several groups at Illinois and Argonne who specialize in single crystal and thin film growth of strongly correlated materials.

FY 2014 HIGHLIGHTS

(1) Discovery of charge density wave domain walls associated with pressure-induced superconductivity in TiSe_2 : As alluded to above, unconventional superconductivity is nearly always found in the vicinity of another ordered state, such as antiferromagnetism, charge density wave (CDW), or stripe order. This suggests a fundamental connection between superconductivity and fluctuations in some other order parameter. To gain a deeper insight into this phenomenon, we used high-pressure x-ray scattering to study the CDW order in the layered dichalcogenide TiSe_2 , which was previously shown to exhibit superconductivity when the CDW is suppressed by pressure or intercalation of Cu atoms. We succeeded in suppressing the CDW fully to zero temperature, establishing for the first time the existence of a quantum critical point (QCP) at $P_c = 5.1 \pm 0.2$ GPa, which is more than 1 GPa beyond the end of the superconducting region. Unexpectedly, at $P = 3$ GPa we observed a reentrant, weakly first order, incommensurate phase, indicating the presence of a Lifshitz tricritical point somewhere above the superconducting dome. Our study suggests that superconductivity in TiSe_2 may not be connected to the QCP itself, but to the formation of CDW domain walls. This study was published in *Nature Physics*. (2) Improved measurements of the effective fine structure constant of graphene: A few years ago we published a paper claiming that graphene is not a strongly correlated electron system [J. P. Reed, *et al.*,

Science 330, 805 (2010)]. While many theorists were arguing that Coulomb interactions were nonperturbative in graphene, we argued that in most regions of phase space Coulomb interactions are screened out. We quantified this statement by characterizing the strength of interactions in terms of an effective fine structure constant, which we found to have the rather small value of 0.14. This result was met with enough skepticism that we repeated the study with ten times higher energy resolution.

Multifunctional Materials Research Using Ultrafast Optical Spectroscopy

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Students: 1 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding: \$194,000 (2014)

PROGRAM SCOPE

The properties of complex transition metal oxides (TMOs) arise from subtle interplay between competing degrees of freedom. The results are dramatic and include superconductivity, novel magnetic ordering, and metal insulator transitions. Advances in the synthesis, growth, and characterization of complex TMOs coupled with new experimental techniques in ultrafast optical spectroscopy have ushered in an exciting era of dynamics and control in these materials. Our experiments utilize femtosecond optical pulses to initiate and probe dynamics of the spin, lattice, orbital, and charge degrees of freedom. Major goals include determining how interaction and competition between the relevant degrees of freedom determine macroscopic functionality in TMOs and searching for hidden phases in TMOs by controlling dynamic trajectories in a complex and pliable energy landscape. We are currently investigating strained manganites ($\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$), nickelates (NdNiO_3 and EuNiO_3), and vanadates (V_2O_3 and VO_2). These materials exhibit insulator-to-metal transitions and our work is focused on interrogating and controlling the dynamic pathways of such transitions using ultrashort optical and far-infrared pulses. This work directly impacts BES grand scientific challenges including enhancing our understanding of matter far from equilibrium and the emergence of collective phenomena in condensed matter.

FY 2014 HIGHLIGHTS

During FY 2014, we have observed interesting phenomena in several complex transition metal oxides that exhibit insulator-to-metal transitions. In strained $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$, we have discovered a photo-induced metastable transition from a charge ordered insulating state to a ferromagnetic state. In V_2O_3 , the conductivity dynamics of the insulator-to-metal transition exhibit scaling and can be described in terms of nucleation and growth of the metallic volume fraction. This growth occurs ballistically at the speed of sound. Finally, in NdNiO_3 , it appears that the photoinduced insulator-to-metal transition results in conductivity dynamics that closely follows magnetic disordering of the Ni ion sublattice.

Ultrafast Infrared Nano-Spectroscopy and Nano-Imaging of Unconventional Superconductivity in Cuprate and Pnictide High- T_c Systems

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Sr. Investigator(s): Richard Averitt; California-San Diego, University of
Michael Fogler; California-San Diego, University of
James Hone; Columbia University
Andrew Millis; Columbia University
Students: 3 Postdoctoral Fellow(s), 2 Graduate(s), 2 Undergraduate(s)
Funding: \$400,000 (2014)

PROGRAM SCOPE

High- T_c superconductivity is surpassed by few, if any, other unresolved problems in contemporary physics in its richness, complexity, impact on other fields and potential technological importance. A specific common aspect of Fe-based and Cu-based high- T_c superconductors is a propensity towards electronic and magnetic self-organization, leading to dynamic inhomogeneities at nano-to-mesoscopic length scales. The inhomogeneities have so far been documented with quasi-static probes and scanning tunneling microscopies. In contrast, ultrafast infrared/optical studies enable characterization of dynamics and fluctuations in superconductors. However, such experiments have been carried out using diffraction-limited optics and therefore probe length scales that inform us of a “mixed” response involving contributions from the multiple electronic, chemical and structural phases occurring in real materials along with nanoscale heterogeneities. As a result, the interpretation of area averaged ultrafast optics data has been complicated and often ambiguous. We propose an effort to investigate the intrinsic spatio-temporal response of pnictides and cuprates. The goal of the proposed work is to carry out pump-probe infrared (IR) spectroscopy and imaging studies with 10-nm spatial resolution and temporal resolution of tens of femtoseconds. This will be enabled through a unique THz-IR nano-spectroscopy/imaging set-up developed by Basov. Nano-scale IR measurements will be augmented with ultrafast studies of superconductivity using THz pump – THz probe experiments carried out at the group of Averitt. THz/IR nano-imaging of surface plasmons will be performed using ultrathin samples of cleavable cuprate and pnictide superconductors capped with a protective layer of boron nitride prepared in the group of Hone. Theoretical and computational studies of ultrafast electrodynamics in cuprate and pnictide materials will be carried by Millis and Fogler.

FY 2014 HIGHLIGHTS

Since the inception of the program in August 2014, our team has made significant progress with the design and numerical modeling of meta-material antennas intended to enhance photo-induced effects in cuprate high T_c superconductors. These structures are currently being fabricated at Columbia. In parallel, we dedicated significant effort to improving the signal-to-noise ratio of our pump-probe nano-infrared experiments. Novel approaches to data acquisition have allowed us to increase the signal-to-noise up to 1000-5000 nearly matching usual benchmark numbers of conventional diffraction limited measurements.

X-Ray Studies of Highly Correlated Systems

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Funding: \$100,000 (2014)

PROGRAM SCOPE

Our work involves studies of strongly correlated systems using synchrotron x-ray sources. Much of the work involves using inelastic x-ray scattering (IXS) and Resonant Inelastic X-ray Scattering (RIXS) to study electronic and vibrational excitations. A goal of our current work is to measure polarization of the scattered x-ray during RIXS. Scattering can change the energy, wavevector, and polarization of the x-ray. Currently, only the first two are measured. This is unfortunate, since polarization carries valuable information about the states involved in the scattering, including symmetry information. Specifically, we wish to develop polarization analysis for materials with strong spin-orbit coupling such as the iridates. We have previously developed a curved graphite polarization analyzer for measurements at the copper K-edge, but polarization effects are likely to be more interesting at the L- and M- edges.

FY 2014 HIGHLIGHTS

We have been creating and characterizing bent single crystal Si polarization analyzers for resonant inelastic x-ray scattering at the iridium L3-edge. Recently, we have been bending very thin Si single crystal wafers to limit the strain. The Si is bent in a double toroidal shape which is a good approximation to the logarithmic spiral which is the exact shape required to have the curved surface meet the Bragg condition. The advantage of using a good crystal is that it keeps the good energy resolution of the main analyzer. So far, we have been able to achieve resolutions of about 140 meV but only with an efficiency of about 0.5%. We have also carried out measurements and simulations to study the polarization of the incident x-ray synchrotron beam above the plane of the electron beam. We find good agreement with standard models of synchrotron radiation. Characterizing the beam polarization is necessary in order to know the ratio of the initial polarization components, and may also be useful for aligning the polarization analyzer in the polarization flipped channel. We have also carried out studies of the magnetic excitations in BaIrO₃. BaIrO₃ is an interesting 5-d transition metal system. It contains Ir atoms in both quasi 1-d zigzag chains and 2-d planes. It has a combined ferromagnetic and charge density wave (CDW) transition at 180 K, and the system displays unusual non-linear voltage characteristics that may or may not be related to the CDW. We have begun a study of the magnetic excitations in this material throughout the Brillouin zone as a function of temperature.

Electrons, Spins, and Lattice Structures of Surface-Based Nanoscale Systems

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Funding: \$285,359 (2014)

PROGRAM SCOPE

The proposed research focuses on the physics of surfaces, interfaces, and tailored structures that are promising for a wide range of scientific and technological advances in the quantum, nano-, and meso-scale regimes. Measurements, modeling, and computation will be performed to determine and to understand the electronic, spintronic, and atomistic behavior of selected surface-based nanoscale

systems. Electrons confined in nanoscale systems form discrete states, or quantum well states, that are sensitive to the physical dimensions, boundary conditions, and spin-orbit coupling. As a result, the electronic and spintronic properties can exhibit substantial quantum variations (or oscillations) as a function of system size and environment. The lattice structure of the system in turn responds to these changes as a result of electron-lattice coupling, possibly leading to distortions and new lattice structures with different symmetry types. These effects can be pronounced at the nanoscale because of quantum coherence, interference, entanglement, and the relative ease of atomic movement at surfaces. The resulting collective behavior involving coupled electron, spin, and lattice degrees of freedom can deviate substantially from the bulk limit, thus giving rise to ample opportunities for engineering properties and functions by tailored synthesis. The underlying physics principles are of basic importance to nanoscale and mesoscale science and technology, a prevailing national research theme. Our research is directed mainly at four areas: (1) surfaces, interfaces, and ultrathin films involving topological insulators and spin systems, (2) dichroic effects associated with angle-resolved photoemission spectroscopy, (3) coupled electronic and lattice effects on the epitaxial growth of thin films, and (4) phase transformations in oxides. The experimental work will include angle-resolved photoemission spectroscopy and x-ray diffraction and scattering.

FY 2014 HIGHLIGHTS

(1) Interfacial bonding and structure of Bi_2Te_3 topological insulator films on Si(111): Interfacial topological states are a key element of interest for topological systems, and their properties can depend sensitively on the atomic bonding configuration. We employ non-resonant and resonant surface X-ray scattering to study the interfacial and internal structure of a prototypical topological film system: Bi_2Te_3 on Si(111). The results reveal a Te buffer layer, a large interfacial spacing, and a slightly relaxed and partially strained bottom layer of an otherwise bulk-like Bi_2Te_3 film. The presence of the buffer layer indicates a nontrivial process of interface formation and a mechanism for electronic decoupling between the topological film and the Si(111) substrate. (2) Electronic size effects in three-dimensional Bi nanostructures: This research is performed in collaboration with P. J. Kowalczyk (Poland), Mahapatra and S. A. Brown (New Zealand), and X. Wang (China). We show that bismuth nanostructures form three-dimensional patterns governed by two-dimensional electronic effects. Scanning tunneling microscopy reveals that both the vertical and lateral dimensions of the structures favor certain values and that the preferred widths are different for each preferred height. Calculations demonstrate that this effect is related to the Fermi surface topology, which in turn depends sensitively on the dimensions of the structure. (3) Topological phase transition and Dirac fermion transfer in Bi_2Se_3 films: Topological surface states, while protected by time-reversal symmetry in the bulk, can be missing in films with thicknesses much greater than the decay lengths of the surface states. This novel effect is demonstrated theoretically in Bi_2Se_3 . When the spin-orbit-coupling strength is tuned through the quantum critical point, there is a wide dead zone where the film is topological but without topological surface states. This dead zone can be suppressed by interfacial bonding.

Oxide Interfaces: Emergent Structure and Dynamics

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Principal Investigator: Roy Clarke
Sr. Investigator(s):
Students: 1 Postdoctoral Fellow(s), 1 Graduate(s), 3 Undergraduate(s)
Funding: \$176,789 (2014)

PROGRAM SCOPE

The overall goals of this program are focused on the behavior of epitaxial oxide heterostructures at atomic length scales (Ångstroms), and correspondingly short time-scales (fs-ns). We aim to achieve a better basic understanding of structural and electronic correlations and how these can be exploited for technological applications, especially energy conversion and harvesting. Topics of interest include: probing the microscopic behavior of epitaxial interfaces and buried layers; novel materials structures that emerge from ionic and electronic reconfiguration at epitaxial interfaces; ultrahigh-resolution mapping of the atomic structure of heterointerfaces using synchrotron-based x-ray surface scattering, including direct methods of phase retrieval; using ultrafast lasers to study the effects of transient strain on coherent manipulation of multi-ferroic order parameters; and investigating structural ordering and relaxation processes in real-time. Atomic-scale detail can be achieved by direct methods (COBRA), which were used to determine a new ferroelectric heterostructure based on the SrTiO₃ – LaAlO₃ interface.

FY 2014 HIGHLIGHTS

We have studied the thickness dependence of the BiFeO₃ thin film structure in the ultra-thin regime under moderate compressive strain (~ -1.4%) from (001) SrTiO₃ substrates. The samples were prepared in Schlom's MBE lab at Cornell. We found that a structural transition occurs from monoclinic to tetragonal, accompanied by a change in the octahedral tilt pattern when the film thickness is less than 20 unit cells. This definitively establishes the ultrathin-film structure as tetragonal which is important for several reasons: first, device applications normally require a single-domain state, which the lower-symmetry bulk-like monoclinic phases do not generally support; and secondly, the new tetragonal phase favors a polar alignment normal to the plane of the film, a geometry that is favorable for planar devices. The work reveals a novel "untilting" mechanism driven by the epitaxial heterointerface with SrTiO₃, which itself is untilted under ambient conditions. This in turn drives the transition to tetragonal symmetry. The work is published in APL materials. We also studied the effect of epitaxial strain on this structural transition. Samples of BiFeO₃ grown on LaAlO₃ substrates, grown by pulsed laser deposition in the group of Hans Christen at Oak Ridge National Laboratory have a significantly larger mismatch (-4.3%). Interestingly, these highly strained films grown on LaAlO₃ also show the disappearance of the monoclinic peak splitting in the ultrathin regime. The larger compressive stress apparently drives the transition thickness to smaller dimensions, indicating again that the substrate interface plays a crucial role in the formation of the tetragonal phase. We have also studied the structure of these ultrathin samples down to low temperatures (~30K). These studies are ongoing.

Dynamical Control of Nanoscale Order in Complex Oxides

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Funding: \$198,932 (2014)

PROGRAM SCOPE

A series of recent advances now allow materials to be designed and created in which spontaneous nanoscale order arises from a competition between atomic-scale and long-range effects. In nanoscale ferroelectrics, the competition is between structural effects associated with the creation of interfaces and the larger-scale phenomena arising from electrical polarization. Their relative importance can be tuned by varying the spatial extent and composition of the nanostructures. The development of nanoscale order is fundamentally important because it leads to new phenomena, including the formation of polarization domain patterns and local atomic arrangements that profoundly influence phase transitions and functional electronic and optical properties. We focus here on ferroelectric materials in which the balance of long-range and atomic-scale effects is manipulated via the systematic creation of atomic-scale superlattices. In particular, superlattices incorporating a very thin ferroelectric layer spontaneously form a domain pattern with a characteristic repetition length of several nanometers, with profound effects on the functional properties as well on the physics of phase transitions. The configurations of the polarization in the superlattices also include geometric arrangements that are difficult to stabilize in compositionally homogenous materials, including polarization vortices and anti-vortices. The present state-of-the-art in the experimental understanding of the nanoscale domains in ferroelectric superlattices is based on probes which either inform us only about the static state of the system (i.e. corresponding to the dynamics at the very longest times) or which lack nanoscale specificity. A rapid series of experimental developments both in synchrotron x-ray diffraction facilities and in x-ray scattering instrumentation and techniques now make it possible, however, to achieve much better specificity in the study of these phenomena.

FY 2014 HIGHLIGHTS

Our accomplishments are in three areas: 1) Equilibrium Ferroelectric Domain Dynamics: We have used coherent x-ray nanobeam scattering to show that a ferroelectric nanodomain system within a lead titanate/strontium titanate (PTO/STO) thin film heterostructure superlattice exhibits a disordered spatial pattern accompanied by fluctuations of the domain pattern at room temperature. The temporal decorrelation of domains at thermal equilibrium fits a compressed exponential time dependence similar to the thermal fluctuation of soft materials, suggesting that the fluctuation of ferroelectric nanodomains is also driven by the transition between spatially disordered metastable states. 2) Effects of Spatial Confinement on the Geometry of Ferroelectric Striped Domains: We have used a lithographic process based on focused ion beam (FIB) lithography to create nanoscale structures confining the stripe domain pattern in PTO/STO superlattices. The ferroelectric nanodomain pattern within the ridges patterned into the PTO/STO superlattices was studied using coherent microbeam x-ray diffraction. The size of the crystal has a significant effect on the domain scattering, including the distribution of in-plane directions of domain walls. 3) Large Optically Induced Strains in Multiferroics: Working with Dr. Haidan Wen and Dr. Yuelin Li at the Advanced Photon Source we have found that that intense femtosecond laser pulses can induce transient strains of up to 0.5% in multiferroic BiFeO₃ thin films. Our initial results, published in early 2013, have been followed by a systematic study of the magnitudes and time constants of the optically induced strain. Matthias Bargheer (Uni. Potsdam) has shown using laser-plasma x-ray source studies of the same samples that the strain is developed within less than 10 ps following the optical excitation, matching the APS results and published in collaboration with our group.

EARLY CAREER: Optical Manipulation and Detection of Emergent Phenomena in Topological Insulators

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Students: 0 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding: \$175,000 (2014)

PROGRAM SCOPE

The goal of this project is to develop short-pulse laser-based experimental tools to probe the ultra-fast electron dynamics of topological insulators. Topological insulators exhibit a newly discovered property of matter where surface electrons have exceptional conducting properties distinct from the non-conductive nature of the bulk insulator material. This project will develop advanced optical spectroscopy along with electron spectroscopy and diffraction, all based on ultrafast laser pulses as the initial excitation source. The techniques will be developed with the goal to observe the time-resolved signature of quantum interactions and order in topological insulator and related materials.

FY 2014 HIGHLIGHTS

(1) We have implemented high harmonic generation light source for ARPES. We have successfully generated light energies in the region 20-30 eV. We have already used this light source to obtain angle resolved photoemission spectroscopy (ARPES) patterns. (2) We have used the time domain terahertz spectroscopy setup to study graphene. We have demonstrated the ability to control the way light influences the conductive properties of graphene by electrically tuning the number of electrons in the material. We showed that an intense incident light pulse can either increase or decrease the electrical conductivity of graphene, depending on how many electrons are initially in the material. By using ultrashort laser pulses, modulation of conductivity can be controlled in one trillionth of a second. This work also revealed that the conducting capacity of graphene depends on temperature in a manner distinct from that of conventional metals or semiconductors, due to the unique crystal symmetry of this two-dimensional carbon material. These results may potentially be useful for developing next-generation optoelectronic devices using graphene. (Phys. Rev. Lett. 113 , 056602 (2014))

Ultrafast Electronic and Structural Dynamics in Complex Materials

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Funding: \$525,000 (2014-2016)

PROGRAM SCOPE

The goal of this project is to use light to break time reversal symmetry (TRS) to achieve experimental realization of several fascinating effects in 3D topological insulators (TIs). First, we hope to achieve a complete understanding of the nature of Floquet-Bloch states and the photoinduced TRS broken phase

in topological insulators. Then, we will use this light induced TRS broken state to realize several theoretically predicted exotic phenomena in TIs. In particular, we will search for light induced quantum anomalous hall effect, low frequency magneto-optical effects and one-dimensional chiral edge modes. This new field of Floquet physics in TIs is ripe for exploration, the importance of which extends well beyond understanding topological materials. The ability to change electronic band structure with light could fundamentally change the way we think about generating materials with novel properties.

FY 2014 HIGHLIGHTS

Observation of Floquet-Bloch states on the surface of a topological insulator. The unique electronic properties of the surface electrons in a topological insulator are protected by time-reversal symmetry. Using time- and angle-resolved photoemission spectroscopy, we show that an intense ultrashort mid-infrared pulse with energy below the bulk band gap hybridizes with the surface Dirac fermions of a topological insulator to form Floquet-Bloch bands. These photon dressed surface bands exhibit polarization-dependent band gaps at avoided crossings. Circularly polarized photons induce an additional gap at the Dirac point, which is a signature of broken time-reversal symmetry on the surface. These observations establish the Floquet-Bloch bands in solids and pave the way for optical manipulation of topological quantum states of matter. 'Observation of Floquet-Bloch States on the Surface of a Topological Insulator' Y.H. Wang, H. Steinberg, P. Jarillo-Herrero and N. Gedik Science 342, 453 (2013).

Dynamic Visualization and Control of Emergent Phases in Complex Oxide Heterostructures

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Funding: \$818,398 (2014)

PROGRAM SCOPE

Our project aims to address two of the grand challenges of materials research put forth by the BES, namely to uncover hidden phases in transition metal oxides by controlling dynamic trajectories in a complex energy landscape by preferentially exciting specific degrees of freedom, while developing the experimental and theoretical tools to control matter away from equilibrium. We propose an interdisciplinary team to explore the physics of transient and metastable states in complex oxide films and heterostructures at ultrafast time scales studying two broad classes of phenomena: strongly electron correlated oxides exhibiting metal-insulator transitions, and "hidden phases" in ferroelectrics and multiferroics. Fundamental research goals that will be addressed by the team are to: (a) Establish

materials design principles beyond the ground state paradigm to control and tailor material responses at ultrafast time scales. (b) Identify phase competition mechanisms to stabilize phase coexistence and engineer enhanced susceptibilities. (c) Use spatio-temporal methods to gain new insights into creation and destruction of phases that arise from strongly competing interactions. In order to probe transient states, the team has assembled experts in a new generation of ultrafast and ultrabright light sources in terahertz, infrared and hard X-ray free electron lasers, as well as pioneers in the development of nanoscale diffraction, spectroscopy, and ultrafast multimodal microscopy techniques such as ultrafast infrared near-field nanospectroscopy. The team consists of experienced users and resident scientists at national X-ray user facilities including the Linac Coherent Light Source (LCLS) and the Advanced Photon Source (APS). They are complemented by material growers, who utilize state-of-the-art hybrid and laser molecular beam epitaxy with unit cell level control, and theorists who bring materials-by-design density functional and non-equilibrium dynamical mean field theory.

FY 2014 HIGHLIGHTS

We have discovered a hidden ferromagnetic state in (La, Ca) MnO_3 films in paramagnetic insulator state through optical excitation at 1.55eV and THz time domain spectroscopy (Averitt, Basov). We are setting up optical-pump THz-probe and optical pump x-ray probing studies of strained manganites and strained vanadate films (Averitt, Wen, Freeland, Chakhalian). We are performing ultrafast nanospectroscopic microscopy on VO_2 thin films (Basov). Ultra-fast, pump-probe studies of BiFeO_3 films reveal metastable excited states under ultra-fast, high electric pulses (Martin, Wen, Freeland collaboration with A. Lindenberg, Stanford). We have discovered metastable phases in BaTiO_3 (Gopalan) and are performing optical/THz pump – X-ray probing of titanates and vanadates (Gopalan, Wen, Freeland, Martin, Engel-Herbert). In strained Nickelate films, we have discovered that structural and electronic orders can be disengaged (Chakhalian, Freeland, Averitt). Using DFT (Rondinelli), we have determined ground state structure of LaSrMnO_3 under epitaxial strain constraint. The next step is to compare the electronic/magnetic properties to those determined in experiment. Vibrational frequencies for CaTiO_3 and LaTiO_3 have been computed. The coupling constants connecting the mode displacements describing IR-active and TiO_6 Raman modes have been computed. We are exploring the dependence of rotation amplitude, correlation, and A-cation size on the strength of the interaction. Already, we find that the interaction is strongly dependent on the d electron count. The electronic structure of the metastable states has also been computed and is being explored in more detail. We are developing the theoretical machinery needed to do time dependent dynamical mean field theory (Millis).

Synchrotron X-ray Based Electronic Structure Study of Correlated Quantum Materials and Topological Insulators

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Funding:	\$366,000 (2014)

PROGRAM SCOPE

Novel electronic phases, excitation modes, and phase transitions in quantum materials are topics at the forefront of modern fundamental condensed-matter physics. Research in these areas has led to new

superconductors and thermoelectric and spintronic materials, which have uses in future electronic, information and energy technologies. At Princeton, the P.I. leads the ARPES and x-ray spectroscopy work that combines synchrotron x-ray based techniques of photoemission spectroscopy and x-ray scattering to gain critical insights about the complex electronic structure of novel quantum materials. The main goal of this program is to investigate the ternary and quaternary-complex topological insulators and iron pnictide high T_c superconductors towards discovering new physics and functionality (both bulk and MBE thin film geometries). Physics topics that are being covered include systematic study of Topological Phase Transition and dynamics of 3D Dirac Fermions and exotic symmetry breaking phenomena. In addition, some exploratory investigation into non-topological insulator spin-orbit materials featuring novel surface phenomena and/or correlated phenomena such as novel Dirac modes and the Weyl Fermions are underway.

FY 2014 HIGHLIGHTS

The 3D topological Dirac semimetal systems with strong spin-orbit coupling can host many exotic Hall-like phenomena and Weyl fermion transport. Using high-resolution ARPES, we performed electronic studies of Cd_3As_2 and Na_3Bi which have been predicted to be the parent material, from which many topological phases can be derived. We experimentally identified their 3D topological metallic nature. Our discovery of the Dirac-like bulk topological semimetal phase in Cd_3As_2 and Na_3Bi opens the door for exploring higher dimensional relativistic physics. [S.-Y. Xu, C. Liu et.al., Observation of Fermi arc surface states in a topological semimetal; *Science* 10.1126/science.1256742 (2014) and Observation of a 3D topological Dirac semimetal phase in high-mobility Cd_3As_2 ; M. Neupane et.al., *Nature Commun.* 5, 4786 (2014) and *Nature Commun.* 5, 3841 (2014).] Superconductivity involving topological Dirac electrons has recently been proposed as a platform between concepts in high-energy and condensed-matter physics. It has been predicted that supersymmetry and Majorana fermions, both of which remain elusive in particle physics, may be realized through emergent particles in these particular superconducting systems. Using artificially fabricated topological-insulator–superconductor heterostructures, we presented direct spectroscopic evidence for the existence of Cooper pairing in a weakly interacting half Dirac gas. Our studies revealed that two dimensional topological superconductivity in a helical Dirac gas is distinctly different from that in an ordinary two-dimensional superconductor in terms of the spin degrees of freedom of electrons. Our demonstration and momentum-space imaging of Cooper pairing in a half-Dirac-gas two-dimensional topological superconductor serve as a critically important platform for future testing of fundamental physics predictions such as emergent supersymmetry and topological quantum criticality. [S.-Y. Xu et.al., *Nature Physics* 10, 943 (2014)]

Understanding Valley Spin Coupling and Two-Dimensional Exciton Gases in Layered Materials at Extreme Magnetic Fields

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Funding:	\$455,727 (2014)

PROGRAM SCOPE

The advent of graphene has generated a wealth of interest in other materials that can be made two-dimensional (2D). Atomically thin group VI transition metal dichalcogenides (TMDs) have emerged as one of the most interesting and important classes of 2D materials beyond graphene. When reduced to a monoatomic layer thickness, they exhibit drastic changes in the electronic properties, exhibiting a crossover from an indirect gap in the bulk to a direct band gap semiconductor. Also, as is common for lower-dimensional materials, many-body interactions are found to be significant, forming strongly bound excitons and trions. Although these quasiparticles have been observed, their properties are not well studied. These materials are important for numerous applications, central to the DOE's mission. Most electronic devices exploit the electric charge of electrons, but it is also possible to build devices that rely on other properties of electrons. Spintronic devices, for example, make use of the spin of electrons. 'Valleytronics' is a more recent development that relies on the fact that the conduction or valence bands of some materials have two or more degenerate minima/maxima at different positions in momentum space. Group VI TMDs are a promising material for valleytronics. In large magnetic fields monoatomic layers III-VI chalcogenides, undoped or doped behave similar to two-dimensional electron gases formed in modulation doped systems or graphene. The formation of Landau levels in high magnetic fields and the confinement of electrons and holes have led to the observation integer and fractional quantum Hall effects. Inspired by fascinating and not yet understood effects observed in modulation doped systems, we will investigate these effects in this novel class of two-dimensional materials at extremely high magnetic fields. At these extreme magnetic fields we will apply the most advanced ultrafast techniques including multidimensional Fourier-transform spectroscopy.

FY 2014 HIGHLIGHTS

'Biexciton formation and exciton coherent coupling in layered GaSe' P. Dey, J. Paul, G. Moody, C. E. Stevens, N. Glikin, Z. D. Kovalyuk, Z. R. Kudrynskyi, A. H. Romero, A. Cantarero, D. J. Hilton, D. Karaiskaj, submitted for publication.

EARLY CAREER: Generation, Imaging, and Control of Ultrafast Electrical Currents and Radiation

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Funding: \$150,000 (2014)

PROGRAM SCOPE

The PI investigates the physics of ultrafast electrical current and electromagnetic radiation generation/control in two systems: (a) centrosymmetric gaseous plasmas and (b) symmetry broken gaseous plasmas and solid-vacuum boundaries. In these systems, the PI uses ultrashort optical laser pulses to produce and control ultrafast electrical currents, as well as, to study the current evolution, screening, and decoherence with accompanying electromagnetic radiation. In particular, coherent broadband terahertz (THz) emission, expected from fast arising current surge, is of great interest and can be a useful tool for studying the underlying physics of ultrafast currents. Moreover, concurrent or delayed second or third harmonic radiation can provide phase-sensitive nature of current generation

and two-dimensional (2D) imaging of time-varying current density distribution at micrometer-scales. Specifically, in (a), the PI investigates the generation mechanism of ultrafast current via two-color photoionization, recently proposed by the PI, by directly measuring the photoelectron spectrum and linking it with far-field THz and harmonic generation. In terms of producing THz radiation as a potential source, the PI tests the feasibility of achieving an unprecedented millijoule level of THz radiation with a multi-terawatt laser system. Such radiation will allow the observation of extreme nonlinear THz phenomena in a university laboratory. Moreover, our high-energy (multi-microjoule), broadband (>20 THz) THz generation scheme at 1 kHz has potential for studying THz-driven nonlinear optics and spectroscopy.

FY 2014 HIGHLIGHTS

(1) Microscopic mechanism of terahertz generation in two-color photoionization: The primary research goal is to verify the microscopic mechanism of terahertz (THz) generation in two-color photoionization. Although such a source is widely used for many applications, the details of the mechanism are still on debate. Here we have confirmed that the optimal relative phase for THz generation is ~ 90 degrees, not significantly affected by gas species, laser intensities, and intensity ratios between two-color laser fields. These results are in accordance with the semi-classical plasma current model. We have also observed a strong correlation between microscopic photocurrents and resulting THz radiation. This verifies plasma currents as a microscopic source for far-field THz radiation in two-color laser-produced plasmas. In addition, our method of phase measurements can be readily applied to other two-color coherent control systems such as photocurrent production in semiconductors and on metal surfaces, as well as high-harmonic generation and dissociation of molecules in intense two-color laser fields. (2) High-average, high-peak power THz field generation: We have demonstrated strong-field (>8 MV/cm), high-peak-power (12 MW) THz generation with a bandwidth of >20 THz via two-color laser filamentation. Moderate average power (1.4 mW) is also achieved by using a cryogenically-cooled Ti:sapphire amplifier capable of producing 30 fs, 15 mJ pulses at a 1 kHz repetition rate. For maximal THz generation and transmission, we have used a combination of a thin dichroic waveplate and a large Brewster-angled silicon filter. In particular, we have used a microbolometer camera for real-time THz beam profiling and imaging. This cost-effective THz camera along with our intense THz source can be a useful tool for nonlinear THz studies including broadband THz spectroscopy and imaging.

Real-Time X-Ray Studies of Surface and Thin Film Processes

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Funding: \$89,585 (2014)

PROGRAM SCOPE

Surface growth processes are at the core of many of our most widely used technologies today and increasing interest in the “digital design” of future materials for enhanced functionality can only come to fruition if we understand and learn how to control materials synthesis at surfaces and interfaces. The development of increasingly powerful x-ray sources and the new techniques they enable can have a major impact on our understanding and ability to control growth. In particular we are developing

coherent grazing-incidence small-angle x-ray scattering (co-GISAXS) as a powerful new tool for investigating surface and thin film growth dynamics. Coherent x-ray scattering offers the unique promise of being able to elucidate the dynamics, rather than just the spatially-average kinetics, of surface growth processes. As an example, if we consider the typical growth of an amorphous or polycrystalline thin film, the spectrum of surface fluctuations grows during deposition until a steady state is reached. Dynamic processes of deposition and local relaxation continue on the surface but there is no longer any ensemble-averaged kinetics. However it is the dynamic balance between roughening and smoothing processes that is determining the final nanoscale morphology of the growing film. Temporal information about these processes is not accessible in traditional time-resolved x-ray scattering but it is now possible to determine their nature for the first time using the new co-GISAXS technique.

FY 2014 HIGHLIGHTS

We have continued to make major progress in developing coherent grazing-incidence small-angle x-ray scattering (co-GISAXS) as a powerful new tool for investigating surface and thin film growth dynamics. For our first experiments we investigated room-temperature growth of a-WSi₂ and a-Si films. Data were collected both during the initial phase of film growth and during the later stages, when the spectrum of surface height fluctuations reached a dynamic steady state. The scattering growth to a dynamic steady state saturates first at high wavenumbers. The two-time correlation function at a given wavevector shows growing correlation times until a steady state, constant correlation time is reached. In this late stage there is no longer any ensemble-averaged kinetics, and hence there is no temporal information to be obtained from a conventional scattering experiment. However local dynamics of deposition and relaxation continues and it is these processes which are determining the final nanoscale morphology of the growing film. For conditions in which significant scattering signal comes from the bulk of the film, oscillations are seen in the autocorrelation function indicating a very interesting heterodyning process. In heterodyne processes there is a beating of the sample scattering against a reference signal. Here the reference signal appears to be coming from the internal nano- and micro-structure of the film. Autocorrelation functions of the coherent scattered intensity show compressed exponential behavior with exponents of 1-2 that vary systematically with wavenumber. The correlation times decrease as a power law with increasing wavenumber and the power law exponent is the dynamic scaling exponent z . These exponents are predicted by different theoretical models of the surface evolution and thus the co-GISAXS studies allow direct comparison with competing theoretical predictions.

HPCAT -- An Integrated High-Pressure Facility at the Advanced Photon Source

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Funding:	\$1,213,315 (2014)

PROGRAM SCOPE

The primary goal of this project is to advance high-pressure materials science using the high energy x-ray source at the Advanced Photon Source. At HPCAT, a number of high-pressure synchrotron techniques has been developed and widely used for the research in discovering new materials and characterizing

novel properties of materials at extreme conditions. HPCAT has played pioneering roles in enabling many of these new capabilities and in establishing new ways of conducting experiments. A broad range of pressure conditions, including both static and dynamic, together with extreme conditions of temperature, radiation, and deviatoric stress, has been integrated with x-ray diffraction, x-ray scattering and spectroscopy, and x-ray imaging techniques. The integrated HPCAT facility allows for extreme condition studies in: (1) structural determinations at various scales from amorphous, nano-, polycrystalline, single crystal, to microstructures of composite materials, (2) measurements of phonon dynamics, charge dynamics, and electronic and spin states of metals, alloys, oxides, nitrides, hydrides, new superconductors, and new superhard or other super-durable materials, (3) *in situ* measurements with high spatial resolution (1-3 microns) and high temporal resolution (down to 100 ps). The powerful, integrated probes at HPCAT and other APS beamlines enable us to tackle a number of grand challenges in high pressure materials science. Some are century-old questions that have finally become within our grasp; some have global impacts that will alter various fields; some are surprising, novel phenomena that will rewrite conventional wisdom. The current objectives of this project are on the four thrust areas: (a) hydrogen and alkali metals, (b) magnetic and superconducting materials, (c) high pressure melting and polyamorphism in liquids, and (d) enabling high pressure x-ray techniques.

FY 2014 HIGHLIGHTS

In the FY 2014, a multigrain diffraction technique has been developed, which has shown to be promising for detail crystallographic information for samples at extreme conditions and holds great potentials for future high pressure crystallography. A new focusing device providing 1-2 micron x-ray beam has been successfully commissioned for megabar x-ray spectroscopy experiments. The developed fast radiographic imaging enables determinations of ultra-low viscosities of liquids and fluids. A new x-ray method based on phase contrast imaging has been successfully used for identifying liquid-liquid immiscibility. Fast (un)loading devices have been coupled with the time resolved x-ray techniques for studying phase transition kinetics and metastability under high strain rates. A new reliable melting criterion has been developed for measuring melting curves of metals. These new capabilities, together with the other already established techniques, are used for studying materials behavior at extreme conditions. Among others, new superconductors were found in metallic and metal oxides. Interesting electronic structures tuned by pressure have been monitored by x-ray spectroscopy. Novel chemistry of the elements has been revealed at high pressures. Liquid-liquid phase transitions have been observed by x-ray diffraction and x-ray imaging. Universal power law has been established for metallic glasses. HPCAT continues to stay among the most productive sector at the Advanced Photon Source in terms of the number publications in “high-impact” journals as well as the total number of publications.

Ultrafast Magnetization Dynamics and Spin Transfer Probes by Coherent Soft X-Rays

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Funding: \$475,000 (2014)

PROGRAM SCOPE

A detailed understanding of nanoscale magnetization dynamics for 3d metals has become critical for spintronics-based memories as a low-power, non-volatile, ultrafast replacement for DRAM and SRAM in ubiquitous computing applications. However, we only have a crude understanding of magnetization dynamics of the transition metals because a comprehensive, self-consistent, microscopic model for metals that rigorously includes the spin, electronic, photonic and phonon-degrees of freedom and their interactions does not yet exist. While the fundamental length- and time-scales for magnetic phenomena are nanometers (exchange length) and femtoseconds (exchange splitting), tools that enable the exploration of dynamics at these scales have only recently become available. Our joint JILA-NIST program is exploring the fastest and smallest dynamics in magnetic materials by use of high harmonic generation (HHG) sources.

FY 2014 HIGHLIGHTS

Using HHG sources, we made several advances in uncovering new understanding of spin dynamics on the fastest timescales.[1-3] First, we solved a controversy regarding the microscopic mechanisms contributing to ultrafast demagnetization.[2] Two theoretical mechanisms had been proposed to explain ultrafast laser-induced magnetization dynamics: non-local quasi-ballistic spin-currents and local spin-flip scattering. Spin-currents would remove spin angular momentum from a given layer, whereas local spin-flip scattering results in a direct transfer of angular momentum between spins and lattice. Our data conclusively showed that both spin-currents and spin-flip scattering contribute with similar efficiency to ultrafast demagnetization in these multilayers.[2] Second, in work in collaboration with Oren Cohen's group at Technion, we demonstrated the first bright, phase-matched, extreme UV circularly-polarized HHG and used this new light source for magnetic circular dichroism (MCD) measurements at the M-shell absorption edges of Ni.[3] For decades it was assumed that HHG from atoms was brightest when both the driving laser and HHG fields were linearly polarized. While the use of passive optical components can convert from linear- to circular-polarization, these are far too inefficient to be practical. Using combined blue and red driving lasers with opposite polarity, we showed that circularly-polarized HHG is unique and robust, producing high photon flux. [1] Mathias *et al.*, "Ultrafast element-specific magnetization dynamics of complex magnetic materials on a table-top", invited, J. Electron Spectroscopy and Related Phenomena 189, 164 (2013). [2] Turgut *et al.*, "Controlling the Competition between Spin Transport and Optically Induced Demagnetization in Magnetic Multilayers," Physical Review Letters 110, 197201 (2013).

Fundamental Studies of the Structural Response of Disordered Materials to High P and T

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Funding: \$176,342 (2014)

PROGRAM SCOPE

Understanding and controlling oxide melts is important to technologies where materials are processed via the liquid phase. Increasingly, solutions proposed to a number of technological challenges in the energy sector involve the synthesis and/or use of disordered materials, including liquids, melts, nano- and glassy materials, at extreme conditions. Examples include materials under high radiation fluxes advanced nano-materials for energy storage and conversion clathrates and other materials in contact with sequestered carbon - supercritical CO₂ in reservoirs or the deep ocean, for example, and high energy density materials. Understanding how the atomic arrangements in this class of materials respond to changes in pressure (p), temperature (T) gas loading and high chemical gradients is therefore fundamental to 1) understanding the behavior of these materials under their operating conditions, and 2) deriving general principles applicable to such classes of materials that 3) can be applied to vary conditions of manufacture that 'steer' toward the desired product. Addressing our energy-related problems will therefore involve learning how to vary reaction pathways, including those at extreme conditions, in order to obtain precise information on changes in structural arrangements *in situ*. We combine development of sample cells for *in situ* x-ray and neutron (XN) scattering of key classes of materials under their operating conditions, with innovative data analysis and modeling in order to characterize materials with intrinsic disorder, such as are encountered in nano-, melt, glassy and gas adduct materials. We do this in collaboration with partners in industry (Richard Weber's group at Materials Development Inc., who develops levitation apparatus with the aid of a DOE SBIR grant) at the APS (Chris Benmore) NSLS-II (Eric Dooryhee) and SNS (Jeorg Neuefeind).

FY 2014 HIGHLIGHTS

Our recent PRL publication reveals a general trend that oxide melts and glasses have lower coordination than their crystalline counterparts. Melts with low cation field strength, such as ZrO₂, and UO₂ are found to have a particularly large coordination drop on melting. Our PNAS paper provides a Pressure-Temperature map for predicting the density and pressure where coordination increase occurs in oxide glasses and melts. Our Nature communications paper provides a structural explanation for the viscosity minimum in silicates melts. This unusual behavior, where silicates initially become less viscous (thin) under pressure, is relevant to processes within Earth's mantle. We also collaborated on a recent Nature paper studying liquid water at extremely low temperatures (-40 °C). This is relevant to the debates about the amorphous and liquid phase transitions in water at these conditions, relevant to conditions in clouds and the behavior of water in interstellar space, which is expected to be amorphous. Our most recent Science article reports measurements of the structure of molten UO₂ for the first time; UO₂ is important technologically and to anthropological climate change since it is the fuel used in most nuclear power reactors, yet relatively little is known about the melt due to the very high temperatures (3200 K) and radiation controls required. Alongside this we have collected data on iron oxides and iron silicate melts, combined with control of the oxidation state. Understanding these melts is relevant to the deep Earth, steel production and slag waste. Many of the measurements we perform are difficult, with complex sample environments that can potentially compromise data. We are working closely with the XPD beamline team at NSLS-II to apply modulation Enhanced Diffraction (MED) to our systems.

Element Specific Atomic Arrangement of Binary and Ternary Alloy Nanosized Catalysts in As Prepared and Active State

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Sr. Investigator(s):
Students: 2 Postdoctoral Fellow(s), 4 Graduate(s), 0 Undergraduate(s)
Funding: \$201,119 (2014)

PROGRAM SCOPE

Project aims at: i) synthesizing a series of technologically important binary and ternary nanoalloy catalysts ii) determining their atomic-scale structure and how it evolves under realistic reaction conditions by *ex situ* and *in situ* high-energy x-ray diffraction (XRD), including element specific resonant XRD, coupled to atomic pair distribution functions (PDF)s analysis and 3D structure modeling, iii) revealing synthesis – atomic structure – catalytic properties relationships in the nanoalloys iv) using the unique knowledge obtained as a feedback loop for streamlining their synthesis with respect to the catalytic properties targeted for optimization thus drafting a roadmap to producing nanoalloy catalysts by rational design. Outcomes: Besides advancing the frontiers of nanocatalysis, the project will push forward high-energy synchrotron XRD and atomic PDFs analysis, in particular resonant XRD, provide new hardware (e.g. reaction chambers) for in-situ high-energy XRD studies of catalytic reactions and perfect 3D structure modeling of nanometer-size materials, such as nanoalloy catalysts, of DOE interest.

FY 2014 HIGHLIGHTS

Major impact of the studies within fiscal year 2014: i) A prime example of a roadmap to synthesis of nanoalloy catalysts by rational design was demonstrated (paper # 5 of the list below) ii) An approach to solving the atomic structure of nanoalloys was put forward (paper # 2 of the list below). iii) A fuel cell reaction chamber was designed and used for *in situ* studies on the structural evolution of cathode catalysts during heavy operation. The chamber may be reproduced or just borrowed and used by other groups interested in similar studies. iv) Unique resonant XRD studies on the structural characteristics of core-shell interface in nanoalloys were carried out. v) Two more research groups, one from Argonne and the other from University of Mississippi, were introduced to resonant high-energy XRD thus helping the community using this technique grow. Indeed, Sector 1 at APS would like to host resonant high-energy XRD experiments on a more regular basis. Sector 6 at APS expressed similar interest. Forthcoming experiments (Pd and Ru K edges) will show which way resonant XRD aimed at atomic PDFs studies at Sector 6 will go. Seven papers published: [1] ACS Catal., 2014, 4, 1859; [2] Nanoscale, 2014, 6, 10048; [3] Phys.Chem.Chem.Phys., 2014, 16, 18866; [4] Chem. Commun., 2014, 50, 6005; [5] J. Am. Chem. Soc. 2014, 136, 7140; [6] RSC Advances, 2014, 4, 42654; [7] Catal. Sci. Technol., 2014, 4, 3570. Two more papers were submitted for publication and 13 presentations (talks plus posters) made.

Nanoscale X-Ray Imaging and Dynamics of Electronic Magnetic Materials

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Funding: \$185,000 (2014)

PROGRAM SCOPE

This proposal is aimed at development and application of several Coherent X-ray Scattering Tools. Our group has made several important developments in Coherent X-ray Diffraction Imaging (CXDI) techniques and have applied them to both stand-alone, isolated nanostructures (nanowires, nanoparticles), and extended objects, such as magnetic thin films (GdFe), as well as applied these methods for in-situ studies of energy storage materials.

FY 2014 HIGHLIGHTS

We have recently developed CXDI technique and applied it to study in-situ ionic diffusion within a single grain of a Lithium Ion battery cathode. By mapping out displacement field and electron density for the same grain in three dimensions, we were able to study how ion distribution is modified during charge and discharge processes. We were also able to see formation of dislocations and their dynamics within Lithium oxide material. We have applied CXDI to studies of curvature-induced strain and stacking faults in metal nanoparticles. We have also recently done the first X-ray Photon-Correlation Spectroscopy experiments at the Free Electron Laser Facility (LCLS) at SLAC. Finally, we have performed ultrafast pump-probe studies of Charge Density Wave in Antiferromagnetic Chromium (associated with formation of Spin Density Wave). All of these results have either been published or submitted over the fiscal year 2014.

EARLY CAREER: Photon-Electron Interactions in Dirac Quantum Materials

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Funding: \$150,000 (2014)

PROGRAM SCOPE

The objective of this proposal is to understand and control electron, photon, and phonon interactions in new classes of Dirac quantum materials, such as graphene and atomically thin transition metal dichalcogenides (TMDs), for new energy harvesting technologies. These materials have unusual physical properties which allow us to probe unprecedented quantum phenomena otherwise not assessable in other material systems. Graphene is a gapless Dirac material with linear energy momentum dispersion for low energy carriers. It has unusual quantum Hall effects with large Landau level spacing, which enables us to investigate non-equilibrium carrier dynamics in the quantum Hall (QH) regime. Monolayer TMDs have a honeycomb lattice structure like graphene. This fact gives them analogous Dirac-like electronic valleys at the corners (K-points) of the hexagonal Brillouin zone. A key difference from graphene is that TMDs possess inversion asymmetry, which gives rise to direct band gaps in the visible regime and non-trivial Berry-phase related physics. But more profoundly, $\pm K$ valleys have circularly polarized optical selection rules, providing the first solid state system for dynamic control of the valley degree of freedom. A second important difference, arising from the transition metal, is large spin-orbit coupling which spin-splits the valence band by 150 - 450 meV.

FY 2014 HIGHLIGHTS

In the current funding period, we made the following progress. (1) In bilayer WSe_2 , we discovered a new coupling effect between spin, valley, and layer pseudospins. Here, both spin and valley degrees of freedom are associated with magnetic moments. The layer degree of freedom is associated with electrical polarization, which corresponds to electrons either in the upper or bottom layers. We showed the electrical control of spin splitting without the applied magnetic fields. Further, we demonstrate the optical generation of valley quantum coherence using interlayer trion states. (2) We designed a monolayer WSe_2 p-n junction and observe bright electroluminescence from the p-n junction area. We identified that the light emission is from the radiative combination of excitons and trions localized at valleys. These excitons are created by strong Coulomb interaction between electrically injected electrons and holes. (3) We demonstrated hetero-epitaxy growth of seamless lateral heterostructures in an atomic plane by physical vapor transport method. Remarkably, each large crystal exhibits two concentric regions with different optical contrast. We identified that the inside and outside triangles are $MoSe_2$ and WSe_2 , respectively. High-resolution transmission electron microscopy image showed that all the atoms lie on a single honeycomb lattice. There are no dislocations or grain boundaries, and negligible distortion of the lattice near the interface, i.e., perfect lateral epitaxy. We showed that the photoluminescence from the heterojunctions is brighter than the bulk, highlighting the interesting optical properties of a 1D heterojunction.

Ultrafast Control of Emerging Electronic Phenomena in 2D Quantum Materials

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Funding: \$370,000 (2014)

PROGRAM SCOPE

The objective of this proposal is to combine both theoretical and experimental efforts to investigate valley dynamics and Berry phase effects on ultrafast timescales in novel two-dimensional (2D) quantum materials - monolayer transition metal dichalcogenides (TMDs). Monolayer TMDs are a new class of direct bandgap semiconductors at the truly two-dimensional limit. Their energy bands consist of two degenerate but inequivalent valleys located at the corners of the hexagonal Brillouin zone. Due to the broken inversion symmetry, their low-energy electron dynamics can be described as a pair of Dirac fermions with opposite masses. This leads to a number of valley-contrasting Berry phase phenomena and, consequently, the first solid system for dynamical control of valley degrees of freedom. To achieve the objective, we plan to employ state-of-the-art ultrafast technologies, including femtosecond optical pump-probe spectroscopy, an intense THz apparatus and advanced x-ray facilities at the Advanced Photon Source (APS), and the ultrafast x-ray facility at Linac Coherent Light Source (LCLS). Part of our proposed work will represent the first ultrafast x-ray study of atomically thin TMDs. Below are the two inter-related tasks. In the first task, we will investigate the dynamics of valley excitons and control of their Berry phase by optical pumping and subsequent manipulation by an intense THz optical field. In the second task, we will investigate the effects of structural deformation on valley quantum dynamics as

well as Berry phase related quantities, which represents control of valley contrasting physical properties by manipulating the time-dependent basis of the electronic wave function.

FY 2014 HIGHLIGHTS

We have started the project from Sept, 2014. In the first period of this project, we focused on the characterization of x-ray response of monolayer transition metal dichalcogenides and their heterostructures. The x-ray experiment is performed at Argonne national lab by Haidan Wen (a Co-PI of the project). We successfully characterized the structural properties of monolayer WSe_2 and identified the fluctuations of the separation between monolayer and sapphire substrates. We have also applied full-field X-ray diffraction microscopy to image the $MoSe_2$ - WSe_2 heterostructures. These initial works are important steps towards the investigation of structural dynamics of monolayer structures using ultrafast x-ray techniques.

DOE National Laboratories

Towards Understanding and Control of Nano-Scale Fluctuations in Strongly Correlated Electron Systems

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Funding: \$1,163,000 (2014)

PROGRAM SCOPE

To advance our understanding of the role of nanometer sized inhomogeneities, nano-phase-separation, and nano-scale stripe features, generically referred to here as “fluctuations”, in determining the properties of strongly correlated electron systems. The approach is to develop state of the art diffraction approaches to study nanometer scale structures, principally around the atomic pair distribution function (PDF) technique, and then to apply these to study fluctuations in electronic systems. Another critical aspect of the project is to integrate scattering with complementary techniques. Nanoscale fluctuations are difficult to study but crucial to understanding the emergent properties of complex materials such as high- T_c superconductivity in oxides, chalcogenides, colossal magnetoresistance and relaxor ferroelectricity - precisely the phenomena that make correlated electron systems so exciting. Techniques include x-ray and neutron diffraction, scanning tunneling microscopy and spectroscopy, electron microscopy and spectroscopy and oxide MBE synthesis. The varied information provided by these techniques; real and reciprocal space, static and dynamic, surface and bulk, will allow us to construct a more coherent view of the fluctuations and their role in the strongly correlated physics of these materials. Once the role of fluctuations in determining these properties is understood it will become possible to explore approaches to control the fluctuations to yield desired properties.

FY 2014 HIGHLIGHTS

(1) Demonstration and characterization of fluctuating SRO stripes above T_{co} in nickelates. PRL 2013. (2) Development of computed tomography atomic pair distribution function analysis, ctPDF. Nature Communications 2013.

EARLY CAREER: Probing the Magnetic Excitations in Complex Oxide Interfaces and Heterostructures

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Funding: \$500,000 (2014)

PROGRAM SCOPE

Heterostructures of transition metal oxides exhibit numerous novel properties that emerge at the interface of such unconventional materials. The microscopic origin of these properties is poorly understood. This program aims to measure the charge, magnetic, and orbital excitations at these interfaces. These excitations provide detailed quantitative information about the parameters at transition metal oxide interfaces and by studying these parameters we aim to understand and eventually control these novel emergent phenomena. In order to do this, we use advanced x-ray scattering methods at synchrotrons such as the National Synchrotron Light Source (NSLS) II at Brookhaven National Laboratory, as well at numerous national and international facilities. We are working to further enhance our abilities to probe these excitations by developing instrumentation to measure the polarization, as well as the energy loss, of the scattered x-ray photons. The goal of the program is to obtain a detailed understanding of the role of interfacial effects such as charge transfer, strain, orbital reconstruction and exchange bias in determining magnetic interactions. This is a vital step towards exploiting these effects to obtain the desired properties for next generation functional devices.

FY 2014 HIGHLIGHTS

This program started on July 15, two and a half months before the end of FY 2014. In this time we established a collaboration with Anand Bhattacharya at Argonne National Laboratory to synthesize and characterize nickelate-based heterostructures. Successful beamtime proposals were awarded time at the Advanced Light Source and the Swiss Light Source for performing Ni M- and L-edge resonant inelastic x-ray scattering (RIXS) experiments on these films. A Bruker D8 Discover diffractometer was procured by the X-Ray Group in order to characterize thin film heterostructures and a postdoctoral researcher was hired to start in November 2014. The PI also prepared a Partner User Proposal for the Soft Inelastic X-Ray (SIX) beamline at NSLS-II. We completed the conceptual design of the x-ray polarimeter for analyzing the polarization of the scattered x-ray photons during a RIXS experiment. We also finalized the parameters for the x-ray multilayer mirrors that form part of this apparatus.

Time Resolved Soft X-Ray Materials Science at the LCLS and the ALS

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Wei-Sheng Lee; SLAC National Accelerator Laboratory
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Funding: \$2,807,000 (2014)

PROGRAM SCOPE

Our efforts are centered on joint theoretical and experimental activities to uncover the origins of phase transitions, non-equilibrium behavior and emergent properties in strongly correlated electron systems with the goal of understanding and potentially controlling emergent phenomena at their natural time and length scales, under equilibrium, non-equilibrium and/or extreme conditions. We explore how quantum mechanics acts at nano- to microscopic length scales and atto- to femto-second time scales, thus enabling the design and optimization of new materials with desirable properties. This is accomplished through the use of high-resolution x-ray spectroscopy and ultrafast pump-probe techniques, with the development of a variety of theoretical approaches to x-ray spectroscopy and non-equilibrium dynamics. Our work is focused on the new capabilities offered at the Linac Coherent Light Source to study novel x-ray spectroscopies in both the time and frequency domains, in equilibrium and in response to tailored light pulse stimuli. We combined that work with other x-ray and optical based activities at other light sources and local laboratories, and utilize DOE tier I computational facilities to carry out numerical investigations. The techniques developed are important to the fundamental understanding of non-equilibrium physical processes and the origin of emergence but also open the ability to control novel properties in materials for energy and other technology applications, resulting in substantial advances of great benefit to DOE.

FY 2014 HIGHLIGHTS

(1) Revealing the asymmetry in collective excitations between electron- and hole-doped cuprates. We used state-of-the-art RIXS instruments to perform momentum-dependent measurements on electron-doped high temperature superconducting cuprates. Surprisingly, upon electron doping, the energy scale of magnetic excitations increases. Furthermore, we also discovered an unexpected branch of collective modes, hinting at the existence of a distinct quantum phase and an associated quantum critical point. Both behaviors of collective modes are distinct from those in hole-doped compounds, demonstrating a notable asymmetry in collective excitations on both sides of cuprate phase diagram. Yet, despite their differences, the persistence of magnetic excitations and the existence of a distinct quantum phase appear to be universal in both hole- and electron-doped cuprates. (2) Low energy excitations from resonant inelastic x-ray scattering (RIXS) at the L-edge in cuprates. We demonstrated that L-edge RIXS can indeed provide a good proxy for measuring the spin dynamical structure factor which complements information obtained from inelastic neutron scattering. Utilizing two numerical techniques, we showed how one can naturally understand the evolution of the spin excitation spectrum with doping and that even in heavily hole-doped compounds these excitations persist at high-energies along the anti-ferromagnetic zone boundary. Our results reconcile recent RIXS experiments with previous investigations using inelastic neutron and Raman techniques; and in addition, we predicted a striking asymmetry between hole- and electron-doped materials, which was recently confirmed in two separate experiments, one by members of the present FWP (the preceding achievement).

Magnetization and Dynamics

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Funding: \$1,355,000 (2014)

PROGRAM SCOPE

The Magnetization and Dynamics FWP focuses on the emergence of mesoscopic spin and charge order in the far from equilibrium states that occur when solid-state devices used for instance in information technology are operated near their speed limits given by the fundamental laws of physics. It aims at addressing the grand scientific challenges related to these areas by developing a fundamental understanding of the evolution of materials properties determined by the flow of energy and angular momentum as the magnetic and charge state is switched by external stimuli. It employs the unique x-ray capabilities at SLAC to access the nm length scale on the complementary fs (LCLS) and few-ps (SSRL) timescales for probing: (1) all-optical magnetic switching in metallic alloys, and (2) electric field driven metal-insulator transitions in strongly correlated materials. The latter makes use of intense THz fields generated by fs lasers and the relativistic electron beams available at SLAC. (3) It finally aims at developing a new generation of non-linear x-ray techniques such as stimulated inelastic x-ray scattering to uniquely probe the electronic and spin interactions in emergent mesoscopic phases.

FY 2014 HIGHLIGHTS

- Investigated all-optical magnetic switching in FeCoGd alloys using elastic resonant magnetic scattering at LCLS, SXR
- Investigated the magnetic domain sizes for the latest generation of magnetic hard disc drives with elastic resonant magnetic scattering at SSRL
- Studied the ultrafast demagnetization of Fe films following fs laser excitation with ultra-violet radiation from the Flash free electron laser
- Investigated the magnetic domain sizes written by fs laser illumination of FeCoTb alloys at SSRL
- Investigated the insulator-metal transition in VO₂ in thermal equilibrium at ALS
- Probed the evolution of the electronic excitations across the metal-insulator transition with Resonant Inelastic X-ray Scattering (RIXS) at the Swiss Light Source
- Investigated the THz driven insulator-metal transition using x-ray scattering techniques at LCLS
- Stimulated inelastic x-ray scattering studies in solid state samples performed at the LCLS AMO beamline
- Studied the laser-induced non-equilibrium phase transition in FeRd films at LCLS, SXR
- Studied the orbital and spin moments of 5 to 11 nm Fe₃O₄ nanoparticles at SSRL.

Synchrotron Radiation Studies

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Dillon Fong; Argonne National Laboratory
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Students: 1 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding: \$2,387,000 (2014)

PROGRAM SCOPE

This program is focused on revealing the underlying equilibrium excitations, reactions, and dynamics that control the properties and evolution of materials for energy. Through innovative use of the Advanced Photon Source (APS) and the Linac Coherent Light Source (LCLS), we are developing and utilizing novel x-ray experimental techniques that will allow the study of phase transitions, synthesis and catalytic processes not only as statistical averages, but as events resolved in both time and space. We explore the competing interactions underlying high T_c superconductivity in order to understand their fundamental physics. We are developing Bragg coherent diffraction imaging techniques, for example “Bragg Projection Ptychography”, and using them to study thin films. We are extending coherent imaging techniques to surfaces and using them to understanding dynamics in the reactive environments of crystal growth and catalysis. Finally, we are performing the first atomic resolution x-ray photon correlation spectroscopy measurements on simple liquids to observe their diffusive and vibrational modes near the glass transition temperature. Throughout this research, we strive to develop a fundamental understanding of materials physics while also laying a solid foundation for in-situ materials science at the DOE Scientific User Facilities. The in-situ techniques enabled by the latest x-ray sources are important components in the transition of materials development from an empirical technology to a control science—a crucial transition if we are to meet the need for new, exceptional materials for energy applications.

FY 2014 HIGHLIGHTS

We developed a new Bragg ptychography technique that reconstructs 3D structural images of a crystal from a set of 2D diffraction patterns measured at a single angle. By integrating concepts from medical computed tomography and coherent diffraction imaging, our new technique can rapidly image a broad range of nanoscale crystals under real-world conditions. We imaged the step structure of buried platinum surfaces (e.g. in an electrochemical cell). The results demonstrated the capability of techniques we’ve developed to apply reflection x-ray ptychography to the study atomic level step structures of interfaces. Using Bragg projection ptychography, we independently imaged nanoscale structural features of a nanoelectronic device prototype at two different Bragg conditions and developed a new analysis approach of the reconstructed images that enabled comparison of experimental distributions of crystal strain and rotation with linear elastic predictions. We performed *in situ* x-ray scattering measurements of SrCoO_{2.5} (001) epitaxial thin films, observing that oxygen is removed from the film in carbon monoxide and is replenished in oxygen. This indicates that carbon monoxide oxidation takes place on this material via the Mars-van Krevelen mechanism. The activity-stability relationship during reaction is then strongly dependent on both the surface exchange coefficient and oxygen diffusivity. We performed the first split-pulse ultra-fast x-ray photon correlation spectroscopy measurements of the q-dependent dynamics in a colloidal liquid. This measurement was made possible by systematic studies of

the performance of detectors at LCLS and by a focused effort to improve the performance of the hard x-ray split and delay instrument at LCLS.

X-Ray Scattering

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Funding: \$1,158,000 (2014)

PROGRAM SCOPE

The central objective of this program is to carry out basic studies of the structural, electronic and magnetic properties of strongly correlated electron systems using advanced x-ray scattering techniques. Particular emphasis is placed on electronic and magnetic structure and phase behavior, on collective excitations and on the investigation of electronic surface and interfacial phenomena. The proposed research has a long term goal of understanding and ultimately controlling the properties of these materials. The program seeks to address questions on the mechanisms of high-temperature superconductivity, the role of intrinsic perturbations in strongly correlated systems and to understand the dynamics over of these systems over a wide range of time and energy scales. Inelastic x-ray scattering and hard and soft x-ray resonant scattering experiments will be carried out as part of a broader effort within the Condensed Matter Physics and Materials Science Department (CMPMSD) and more generally at Brookhaven National Laboratory (BNL) to address these questions. To carry out these objectives, the X-ray Scattering Group also develops instrumentation, and maintains and operates two beamlines at the National Synchrotron Light Source (NSLS) and is involved in the development and use of two sectors at the Advanced Photon Source, and three of the six project beamlines at the NSLS-II.

FY 2014 HIGHLIGHTS

The ubiquity and importance of short-range charge correlations in the cuprate phase diagram has recently become clear. We have used soft x-ray resonant scattering to show that these correlations in the so-called “214” system of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ and in the “123” system $\text{YBa}_2\text{Cu}_3\text{O}_{6.6}$ have order parameters of a similar size, despite having different wave-vectors [1]. Further, we have observed rotated charge stripe ordering for the first time in orthorhombic $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and showed that again this ordering has a similar integrated intensity [2]. These results lend strong support to the idea that there is a common motif to the charge order in all cuprate families. Our ultra-fast experiments on $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$, show that this charge order is melted with a mid-IR photon pump on a time scale of a few hundred femtoseconds [3]. This is much faster than the response of the LTT structural distortion, which in equilibrium is tied to the charge order. This is significant because similar mid-infrared pumps have previously been shown to induce superconductivity in non-superconducting, stripe ordered $\text{La}_{1.675}\text{Eu}_{0.2}\text{Sr}_{0.125}\text{CuO}_4$ and to increase the strength of the superconducting condensate in $\text{La}_{1.875}\text{Ba}_{0.125}\text{CuO}_4$ [4]. Our results are consistent with a picture where, in equilibrium, the charge order inhibits the 3D phase coherence between the 2D planes (even though these have strong superconducting correlations). The mid-IR pump then destroys charge order and allows the formation of 3D phase-coherent superconductivity [4]. Using inelastic scattering, we have also looked for renormalization of the spin correlations as a result of the charge correlations. No such effects were observed [5]. [1] Thampy, *et al.*, Phys. Rev. B 88, 024505 (2013). [2]

Thampy, *et al.*, Phys. Rev. B 90, 100510(R) (2014). [3] Först, *et a.*, Phys. Rev. Lett. 112, 157002 (2014). [4] Nicoletti, *et al.*, Phys. Rev. B 90, 100503(R) (2014). [5] Dean *et al.*, Phys. Rev. B., 88 020403(R) (2013).

Ultrafast Materials Science

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Funding: \$969,000 (2014)

PROGRAM SCOPE

Program is focused around the application of ultrafast techniques to understand and control novel properties and emergent phenomena in complex materials, by: a) resolving in energy, spin and momentum the ultrafast dynamics that results from intrinsic many-body interactions, b) by generating new phases and states that do not occur spontaneously and ultimately, c) by controlling their structural and electronic order via ultrashort light pulses.

FY 2014 HIGHLIGHTS

Our work “Ultrafast Charge Localization in a Stripe-phase Nickelate” was published in Nature Comm. 4, 2643 (2013). As the first ultrafast mid-IR study of a stripe-phase correlated system, it clarifies the initial steps of stripe formation – governed by rapid hole localization and correlated electron-phonon coupling. Understanding stripe dynamics is important for clarifying the role of fluctuating charge order in high- T_c superconductors and other correlated oxides. Optimization and testing of the new extreme ultra-violet time and angle resolved photo-emission spectroscopy (XUV trARPES) setup for initial pump-probe studies of correlated materials, was performed. A paper describing this innovative system is under review in Nature Comm (arXiv:1408.6827). Implementation of reflection-mode THz spectroscopy over an ultrabroadband frequency range was applied to study Cooper pairing and gap dynamics in the high- T_c superconductor Bi-2212, providing important impetus for the imminent XUV trARPES studies of these materials. Similar Ultrafast time-domain THz studies were applied to study the Ni-O bending mode in La-Sr-Ni oxide revealing an intriguing two-component response composed of picosecond phonon splitting (stripe formation) and fast electronic dynamics (pseudogap). This method allows direct access to the charge order amplitude. These new results prelude planned trARPES studies of charge-density wave dynamics. Ultrafast time-resolved ARPES studies of high T_c superconductor reveal a softening of the electron-boson interaction in concomitance with a softening/closure of the superconducting gap. The effect is negligible in the normal state and for a metallic compound, suggesting that the electron-boson interaction might be a booster for pairing in cuprates.

Electronic and Magnetic Structure of Quantum Materials

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Funding: \$2,207,000 (2014)

PROGRAM SCOPE

The overarching goal of this FWP is to understand, and ultimately control, emergent behavior in strongly correlated quantum materials, emphasizing the development and use of novel probes of matter, including scanning probes. During FY 2014 our effort has been largely directed toward experimental and theoretical studies of the electronic structure of intertwined phases in cuprate and ferro-pnictide high-temperature superconductors, and toward probes of the edge/surface states of 3D topological insulators and 3D topological semimetals. Extensive efforts were also devoted to the development of in-situ thin film synthesis coupled with photoemission experiments, with initial focus on FeSe superconductors on SrTiO₃ and MoSe₂ on graphene. This FWP is also developing or modifying several important instruments, such as an upgrade of a synchrotron beamline end station and a new type of time resolved UV laser based photo-emission, including a new modality of spin resolved photoemission.

FY 2014 HIGHLIGHTS

(1) FWP researchers have studied the interplay between the pseudogap and superconductivity in high-T_c cuprate superconductors. The comprehensive ARPES study over a wide temperature and doping range in Bi2212 has revealed an unforeseen antagonistic singularity at T_c in the spectral weight as conclusive evidence for the competition between order parameters for the density-wave-like pseudogap and superconductivity. Theoretical simulations have been performed which confirm the observed singularity is due to this competition. Furthermore, including electron-phonon coupling in the simulation reproduces evolution of the spectral weight and lineshape at the same time on a quantitative level at different dopings/temperatures. The observation of the spectroscopic singularity at finite temperatures over a wide doping range provides new insights into the nature of the competitive interplay between the two intertwined orders and the complex phase diagram near the pseudogap critical point. As a complement, FWP researchers have found a signature for the charge density wave using resonant inelastic x-ray scattering. Such a result is an important step towards defining the crucial parameters for high-T_c superconductivity, and ultimately towards a microscopic understanding and application. (2) FWP researchers have investigated the phase competition in iron-based superconductors. Through systematic studies of the doping and temperature dependence in a model system, including both experimental and theoretical efforts, direct spectroscopic evidence for the microscopic coexistence and competition between superconductivity and magnetic order has been revealed for the first time, providing important insights into the emergence of superconductivity among complex quantum phases. In addition, efforts have been made to elucidate the relationship between the structural phase transition and the spin-density-wave transition in iron-based superconductors, an important issue in understanding phase competition.

Ultrafast Optical Spectroscopy

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Funding: \$150,000 (2014)

PROGRAM SCOPE

The overarching goal of this project is to develop a theoretical framework for understanding and controlling the states that emerge from strong electronic correlations and coupling to bosonic degrees of freedom in strongly correlated electronic materials. The competition between these interactions establishes a delicate balance between emergent states including magnetism, heavy fermion behavior, and superconductivity. However, understanding the microscopic mechanisms governing the emergence of these states remains a challenge. Recently, ultrafast optical spectroscopy has been recognized as a conceptually new approach to tackle this problem. We use a theory-driven, coupled theoretical/experimental approach to explore quasiparticle excitation and relaxation/recombination processes in complex materials. Our theoretical studies focused on developing novel approaches to modeling quasiparticle dynamics in strongly correlated electron materials, including superconductors, heavy fermions, and polaronic materials. We also pursued a series of theory-driven experiments. Specifically, we investigated heavy fermion materials to understand quasiparticle relaxation and recombination in the presence of multiple gaps in the electronic structure, most notably the hybridization gap; multiferroics, as well as heterostructures of materials with competing magnetic/ferroelectric orders, to investigate the role of competition and coexistence of multiple orders; and complex oxides and manganites to study polaron formation and their coupling to other quasiparticles.

FY 2014 HIGHLIGHTS

The design of multilayered complex oxide heterostructures to enhance a specific functionality is an important emerging area in condensed matter physics. Thus, we have also demonstrated that optically pumping carriers across the interface between thin films of a ferroelectric insulator, $\text{Ba}_{0.1}\text{Sr}_{0.9}\text{TiO}_3$ (BSTO), and a ferromagnetic manganite metal can significantly enhance the ferroelectric polarization. This enhancement was detected using second harmonic generation which is proportional to the ferroelectric polarization in BSTO. We find that the photoinduced ferroelectric state remains stable at low temperatures for over one day. This occurs through screening of the internal electric field by the photoexcited carriers, leading to a larger, more stable ferroelectric polarization. These results suggest that ferroelectric/manganite bilayers offer a new avenue for optically increasing and stabilizing ferroelectric order. Recently, we have examined the dynamics at faster timescales using femtosecond time-resolved second harmonic generation, revealing that magneto-electric coupling in BSTO is induced within tens of ps after photoexciting the manganite layer.

III. SCIENTIFIC USER FACILITIES DIVISION

Accelerator and Detector Research

Institutions Receiving Grants

EARLY CAREER: Investigation of Fundamental Limits to Beam Brightness Available from Photoinjectors

Institution: Cornell University

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Principal Investigator: Ivan Bazarov

Sr. Investigator(s):

Students: 0 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)

Funding: \$150,000 (2014)

PROGRAM SCOPE

High brightness electron source R&D is supported by the referenced proposal. That includes manufacturing of a new electron analyzer instrument for studies of the more efficient photocathode materials, experimental and theoretical studies of space charge phenomena that set the limit to the performance of high-brightness accelerators using a test photo injector gun setup. In addition to advancing the area of photoemission-based electron sources and the profound impact it has for the next generation X-ray synchrotron radiation facilities, training of graduate and undergraduate students is an essential part of the project. This is consistent with the growing demand for accelerator physicists in the United States and the world.

FY 2014 HIGHLIGHTS

We have extended the Cornell Monte-Carlo simulation tool for photocathode physics to layered semiconductor structures. This new result was published in Physical Review Letters 112 (2014) 097601 and opens new opportunities for designing superior photocathode structures with very low angle spread in the electrons. A new stand-alone transverse energy measurement system was implemented to allow studies of the intrinsic photocathode emittances at cryogenic temperatures along with the improvements to a comprehensive vacuum chamber, which integrates growth, activation, and characterization of photocathodes in vacuum. The world's brightest beam was demonstrated in 2013 with the help of the photocathodes developed within this award. Superb longevity of the sodium potassium antimonide photocathode was experimentally demonstrated. This result was published in Applied Physics Letters 103 (2013) 103504. A method for advanced laser shaping was implemented, which allows creation of arbitrary electron shapes to minimize the adverse effects on beam brightness from non-linear space charge forces inside the electron bunch. The laser shaping method was theoretically analyzed for its efficiency and then used to create electron bursts in the Cornell high-voltage electron source. This new result was published in Applied Physics Letters 105 (2014) 171109.

Optoelectronic Picosecond Detection of Synchrotron X-rays

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Students: 0 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding: \$313,504 (2014-2016)

PROGRAM SCOPE

The outcome of this research project is a time-resolving x-ray detector that will permit the observation of fundamental physical processes in materials that happen as fast as only one “picosecond,” a billionth of a billionth of a second. This is a natural time scale for many important energy processes at the molecular level that are not easily accessible at the powerful x-ray synchrotron sources where many advanced x-ray studies are currently done. This new detector takes advantage of ultrafast laser pulses to read out the electrical signals generated by x-rays in custom-designed semiconductor devices, produced with state-of-the-art fabrication techniques. Techniques previously developed for optoelectronic applications using semiconductor stripline waveguide circuits will be adapted to synchrotron x-ray pulse excitation. This will include all-optical detection, where the striplines sit directly on optoelectronic crystals that modulate laser pulse polarizations as a function of electric field. This will be accomplished using resources at Purdue University’s Birck Nanotechnology Center as well as Argonne’s Advanced Photon Source. The finished detector will be applied to the science of ultrafast dynamics in complex materials, using laser pump x-ray probe techniques at the Advanced Photon Source. The finished detector will be used to address important questions about ultrafast dynamics, such as non-thermal melting in semiconductors like GaAs and InSb, energy flow carried by vibrations in silicon, and insulator-metal phase transitions in vanadium dioxide and other complex oxides. The successful implementation of this optoelectronic x-ray detector will provide picosecond capabilities to any synchrotron facility around the world, a breakthrough enabling picosecond science to be done “inside” the much longer synchrotron x-ray pulse.

FY 2014 HIGHLIGHTS

We have discovered how fundamental interactions between an x-ray photon and the semiconductor gallium arsenide critically determine the electronic response of the stripline detectors. We found that point defects must be introduced to reduce photocarrier lifetimes, as was well-known from laser studies of similar materials, but for the first time we established that the same point defects produce very different responses from x-rays than optical photons. X-rays produce ballistic photoelectrons and Auger electrons, and we find that these also interact with point defects in ways that were not previously considered. Comparison of detector pulses excited by x-ray pulses versus laser pulses reveal that defects such as the EL2 antisite defect, where an arsenium atom occupies a gallium site and binds a localized electron, in gallium arsenide suppress the creation of electron-hole pairs from x-rays, diverting the energy into other channels. This points the way to more efficient approaches to picosecond detection of x-ray pulses, using optical detection in optoelectronic materials such as lanthanum tantalate, where electric fields are measured directly as opposed to electrical currents. In addition to this fundamental insight, there are two other highlights to report. First, our studies of point defects in gallium arsenide show that x-ray pulses excite metastable states leading to transient energy storage in the EL2 point defects, which can then be interrogated with optical pulses. Second, we have developed an entirely new

approach to measuring the delay time between x-ray and optical pulses with picosecond resolution using frequency domain techniques, which can improve the accuracy of synchrotron-based laser pump x-ray probe experiments.

Versatile, Reprogrammable Area Pixel Array Detector for Time-Resolved Synchrotron X-ray Applications

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Principal Investigator: Sol Gruner
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Students: 2 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding: \$2,850,000 (2013-2015)

PROGRAM SCOPE

It is widely acknowledged that many, if not most, experiments at modern synchrotron radiation sources are limited more by detector capabilities than by the source. This is especially true for time-resolved studies. Examples span many disciplines and include, but are not limited to, material processing; understanding how materials fail; time-resolved protein interactions (e.g., enzymes, membrane proteins, gene regulation); depositions and growth of technologically significant complex films; turbulence in liquids; etc. The goal of this project is to develop a series of silicon-based Pixel Array Detectors (PADs) for challenging time-resolved and structural x-ray synchrotron radiation applications in which flexible data processing hardware are integral to the detector. The front-end detector hardware is comprised of a pixelated semiconductor detector layer that is connected pixel-by-pixel to Application Specific Integrated Circuits (ASICs). Each detector being developed has pixel circuitry tailored for specific categories of experiments for which currently available detectors are inadequate. Thus, the availability of the novel designs that are being developed will considerably expand the scope of experiments that can be performed at synchrotron radiation sources. Since the design and fabrication of custom, large ASICs suitable for area detectors is inherently expensive, it is imperative that each PAD design build on the lessons of earlier work and, in so far as possible, utilize integrated circuit parts that have already been proven to work. Building on prior work of our detector development group, we have been (1) performing R&D on novel PAD designs, (2) adapting pixel circuits developed in the past to new controller hardware to realize usable detectors as rapidly as possible, and (3) demonstrating the resultant detectors by performance of important and novel experimental applications at synchrotron radiation sources.

FY 2014 HIGHLIGHTS

With respect to the approach in the previous paragraph, three PADs under development are a Mixed-Mode PAD (MM-PAD) for ultra-wide dynamic range x-ray imaging, a Keck-PAD for capture of x-ray “movies” at rates of 10 million frames per second, and a MM-PAD variant (called the HDR-PAD) designed for use at x-ray free electron lasers. Highlights include demonstration of the following: (1) The MM-PAD was used to perform 3-dimensional radiographic reconstructions of objects from inherently noisy x-ray images. This is significant because it allows successful radiography in cases where data were formerly thought to be useless. (2) The MM-PAD was used to perform superior x-ray microscopy via the technique of coherent x-ray imaging. This extends the range of x-ray microscopy for examination of nanomaterials. (3) In a first demonstration, a prototype Keck-PAD was to obtain atomic level structural data on the response of metal alloys under conditions of rapid impact by a projectile. The entire

sequence of images lasted only microseconds. This capability will considerably extend time-resolved x-ray studies that have hitherto been unfeasible, and will be especially important in developing impact resistant materials.

Theoretical and Simulation Studies of Seeding Methods

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Funding: \$450,000 (2013-2014)

PROGRAM SCOPE

The main goal of our program is to extend the X-ray FEL capability for exploration of atomic and molecular science, by increasing its peak power by over one order of magnitude. The increase in peak power from the present level of 10-50 GW to 1 TW or more, while maintain good transverse coherence properties, is of critical importance for single particle coherent diffraction imaging, as discussed at a workshop at SLAC in the spring 2014. This peak power level would also enhance the research in nonlinear science. The peak power is increased by seeding or self-seeding the FEL to generate a photon pulse with a narrow energy spread, and an almost flat energy distribution. After reaching saturation at peak power of typically 30 GW, the radiation intensity is further increased by tapering, reducing the undulator magnetic field to adjust it to the electron beam energy to preserve the resonant condition. With this method the energy transfer from the electron to the photon beam increases from about 0.1%, typical value at saturation, to about 5% or more. Another application of high efficiency tapered FELs is lithography. This application requires a high average power FEL, about 10kW or more, operating at a wavelength of about 13 nm. The large efficiency of tapered FELs, combined with a high repetition rate superconducting linac, allows the generation of large average power without the need of an energy recirculating linac, using a much lower electron beam average current, with benefits like a smaller repetition rate for a critical component like the electron gun, and a simpler radiation protection system. Several industrial groups are now considering high average power FELs for the next generation of microchips fabrication facilities. For X-ray FELs dedicated to research the larger efficiency, combined with an optical system to split the photon beam in several less intense beams, can be used to operate simultaneously more than one experimental station, reducing the cost.

FY 2014 HIGHLIGHTS

During 2014 we studied the effect of the transverse electron distribution on the output power of a tapered undulator [C. Emma, J. Wu, K. Fang, S. Chen, S. Serkez, and C. Pellegrini, Terawatt x-ray free-electron-laser optimization by transverse electron distribution shaping, Phys. Rev. ST AB, 17, 110701 (2014)], showing that a uniform or parabolic transverse distribution is more efficient than a Gaussian distribution. We studied for the first time the transverse coherence properties of the radiation from a tapered FEL, using the autocorrelation function approach [C. Emma, C. Pellegrini, J. Wu, K. Fang, S. Chen, S. Serkez, Radiation Properties of Tapered Hard X-ray Free-electron Lasers, in Proc. 2014 FEL Conf. Basel (2014)] and a transverse mode decomposition approach [S.D. Chen, K. Fang, X. Huang, C. Pellegrini, J. Wu, C. Emma, S.D. Chen, S. Serkez, Mode Decomposition of a tapered Free-electron Laser, in Proceedings of FEL2014, Basel, Switzerland]. Good transverse coherence is critically important for

coherent diffraction imaging. Our results show that a tapered FEL maintains good transverse coherence and can be used for imaging experiments. More recently we studied step-wise tapering versus continuous tapering and the effect of reducing the undulator period to decrease the undulator length, and thus its cost [C. Emma, J. Wu, P. Emma, Z. Huang, and C. Pellegrini, Tapering studies for Terawatt level X-ray FELs with a superconducting undulator, in course of publication]. We show that, while continuous tapering is most effective, stepwise tapering, easier to realize, also has good efficiency if the step is of the order of the gain length or shorter. We also show that using a step-wise, short period, less than 2 cm, tapered undulator, and standard LCLS beam parameters, it is feasible to reach peak power in excess of 1 TW at photon energies between 5 and 10 keV.

DOE National Laboratories

EARLY CAREER: Diagonalization Solvers for Electronic Collective Phenomena in Nanoscience

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Principal Investigator: Gonzalo Alvarez-Campot
Sr. Investigator(s):
Students: 2 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding: \$500,000 (2014)

PROGRAM SCOPE

The objective of this project is to study collective phenomena at the electronic level, using the Density Matrix Renormalization Group (DMRG) algorithm, and to develop and make available the corresponding computational codes. The proposed research will be carried out for realistic models of relevance for practical applications of strongly correlated electronic materials. We aim to understand three aspects: the real time evolution in electron transport, the temperature dependence of electronic properties in nanostructures, and the multiscale nature of the emerging orders in strongly correlated systems.

FY 2014 HIGHLIGHTS

We have completed work on the second aim of this project, the study, use, and implementation of temperature-dependent DMRG. The PI has published a paper on minimally entangled typical thermal states or METTS for fermionic systems, and has made available the corresponding codes to the scientific community, as planned in the original FWP. Work on time-dependent DMRG applied to the study of spin-charge separation and similar 1D phenomena in nanostructures has been published in Physical Review. The PI was invited to give a talk at the 2014 March meeting of the APS, and took the opportunity to promote our nanocenter, and to showcase codes and results obtained from work done under this award.

EARLY CAREER: Research and Development of Detection Systems for Neutron Imaging

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Principal Investigator: Philip Bingham
Sr. Investigator(s):
Students: 0 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding: \$2,500,000 (2010-2014)

PROGRAM SCOPE

Neutron radiography (NR) is typically performed in a direct imaging mode (magnification of 1) using scintillator based detectors capable of resolutions in the 50-100 micron range. Neutron optics are not currently feasible for focusing to improve resolution beyond the detector resolutions, so NR systems are designed to place the object as close as possible to the detector resulting in a magnification of one. Such a system design limits the imaging resolution to that of the detector. For magnification with such a pinhole system, the source size is limited to the desired resolution. At the HFIR CG-1D instrument, a common source size is 12mm in diameter, so a magnified setup that achieves 10 micron resolution with a single pinhole would increase exposure time by a factor of 1,440,000. This research effort is focused on development of a Coded Source Neutron Imaging (CSNI) system using magnification to improve resolution without the loss of neutrons associated with a pinhole source. For this system, a mask is positioned between the object and source to produce a source pattern having a known code. The Modified Uniformly Redundant Array (MURA) was previously developed for coded aperture imaging with a 50% open pattern and is being employed for this effort. A coded source mask is a pattern of small apertures with diameters equal to the desired system resolution. In a CSNI system, the recorded image is an overlay of individual radiographs taken by each small aperture in the MURA pattern. Direct deconvolution is traditionally used for reconstruction by correlating the measured projection with a reconstruction kernel specific to the MURA pattern. In this effort, an iterative reconstruction algorithm using a system model that accounts for divergence and source non-uniformities not handled by direct methods is being developed. Key challenges of the effort are manufacturing of the coded mask and development of an iterative reconstruction algorithm.

FY 2014 HIGHLIGHTS

(1) Coded aperture masks have been produced by patterning Gadolinium (Gd) on quartz wafers. Since the quartz wafers are optically clear, mirrored versions of the wafers are being manufactured that will be aligned to double the thickness of the Gd layer in the mask. 10 micron mask resolutions have been repeatedly produced with 9 micron thick Gd and initial tests for 5 micron masks at 4.5 micron Gd thickness have produced usable masks. (2) Quantitative testing of coded source imaging at HFIR CG-1D has been performed using a resolution target manufactured along with the coded apertures. Direct deconvolution reconstructions have shown resolutions down to 20 microns with magnifications above 20x such that the resolution target is placed over 5 meters away from the detector. (3) A methodology and algorithm for measurement of beam nonuniformity and variations in the nonuniformity for each pinhole in the aperture has been developed that captures a few images with larger pinholes and interpolates to model the source distribution for each mask hole. (4) Iterative reconstruction code has been modified to incorporate complex source distribution model.

Detector R&D

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Sr. Investigator(s):	
Students:	1 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	\$800,000 (2014)

PROGRAM SCOPE

The goal of this detector R&D effort is to innovate soft X-ray detection solutions (the overwhelming majority of X-ray detector development in the world today is for hard X-ray detectors) that maximize the scientific reach of the ALS, and to collaboratively improve the state of the art in X-ray detection at other storage ring and FEL-based light sources. Detectors we have developed are in use at ALS, APS and LCLS; and are being prepared for use at NSLS-II and EuXFEL, and potentially several other light sources world-wide. Current R&D efforts are focused on a fine-pitched Charge-Coupled Device (CCD) detector for high resolution Resonant Inelastic X-ray Scattering (RIXS), and increasing frame rates by use of a fully column parallel CCD. In addition, we have demonstrated very thin contacts, essential for high efficiency soft X-ray detection, and are bringing on line an ultra-thin contact process using molecular beam epitaxy (MBE). Lastly, we are leveraging other work in CMOS active pixel sensors and detector thinning to produce CMOS-based soft X-ray detectors.

FY 2014 HIGHLIGHTS

In FY14, we developed a complete electronics and mechanics system for high resolution RIXS. We have also started to deploy CCD detectors with <10 nm thick contacts. For the thinnest contacts, on a larger variety of detectors, we have installed and qualified an MBE-based system, with first detectors expected in FY15. Lastly, we have designed new, high speed clocking electronics for the fully column parallel CCD capable of 10s of kHz frame rates.

EARLY CAREER: Generation and Characterization of Ultra-short Electron Beams for X-ray Free Electron Lasers

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Sr. Investigator(s):	
Students:	1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	\$2,500,000 (2010-2014)

PROGRAM SCOPE

This 5-year project starting from 2010 is to innovate and develop new methods for generating and characterizing femtosecond time-scale electron bunch and x-ray pulses at free-electron laser (FEL) facilities. The x-ray FEL, such as the Linac Coherent Light source (LCLS) at the SLAC National Accelerator Laboratory, has provided a unique tool in many research fields since 2009 with typical pulse durations between 10s to 100s femtoseconds. The x-ray FEL user community is also interested in even shorter x-ray pulses, like a few femtoseconds or attoseconds scale, that would enable many new ultrafast studies such as time-resolved electronic dynamics, with widespread applications in physics, chemistry and biology. Generating ultra-short pulses is a formidable challenge requiring theoretical and experimental breakthroughs to develop new concepts for future design and upgrade of x-ray FEL facilities. An additional challenge is to develop methods to measure the length of ultra-short pulses below 1 fs. The project focuses on two topics: (1) develop new techniques and instruments to characterize femtosecond-scale electron and x-ray pulses; (2) investigate and improve short pulse operation based on the developed diagnostics, and explore new methods to push the short pulse limit down to sub-femtosecond scale.

FY 2014 HIGHLIGHTS

Substantial progress has been made during FY 2014. A recently developed X-band transverse deflector has been ready at the LCLS providing a time resolution below 1 fs rms for soft x-ray FELs (Nature Communications 5, 3762 (2014)). We performed extensive studies with this new tool to understand the lasing process and short pulse generation such as low-charge mode and emittance spoiling-foil scheme. This enables direct time-domain measurement shot by shot for user experiments and demonstrates flexible control of the x-ray pulse duration using the foil scheme. A benchmark study for the deflector method has been performed using a high-resolution spectrometer with excellent agreement has been achieved. With the help of this new diagnostic tool, we have also explored new schemes for short pulse generation, such as a two-bunch operation mode and a new nonlinear compression scheme for attosecond pulse generation.

EARLY CAREER: Large Dynamic Range Beam Diagnostics and Beam Dynamics Studies for High Current Electron LINACs

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Students: 0 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding: \$500,000 (2014)

PROGRAM SCOPE

The goals of this program are to develop new instruments for electron beam diagnostics and use these instruments for beam measurements and studies of beam dynamics that were not possible so far. The main emphasis of the diagnostics development is the significant increase in the dynamics range of the measurements from about 10^3 to about 10^6 . The ultimate goal of the beam dynamics studies is to measure distribution of the beam in transverse and longitudinal phase space with such large dynamic range (LDR). The motivation for this work is the following. On one hand, pulsed, normal conducting, but low average current LINACs provide exceptionally bright beams for the new generation of synchrotron light facilities – the X-ray Free Electron Lasers (FEL). The FEL community is actively working towards extending capabilities of X-ray FELs to high current, high average brightness operation, for instance as the LCLS-II projects intends to do. It is envisioned to accomplish this using Constant-Wave (CW) Superconducting Radio Frequency (SRF) LINACs and increasing the average beam current by many orders of magnitude, while operating with present peak beam brightness. With such large increase in the average beam current and beam power a very small ($\sim 10^{-6}$) fraction of the beam, if not managed and transported properly, can lead to fast degradation of expansive components of the FEL or even to accelerator components destruction, or will prevent required high current operation. When designing, constructing and commissioning such new facilities it is necessary to measure and take in to account fractions of the beam as small as 10^{-6} . This is a non-trivial task. On the other hand, the FEL facility and CEBAF at Jefferson Lab operated with the CW electron beam and large average beam current. This provides the opportunity for the instrumentation development and testing with beam as well as development of experimental techniques, which can be used to understand beam evolution with the LDR.

FY 2014 HIGHLIGHTS

In the past year we made significant progress in improving the dynamic range of the electron beam diagnostics under development. We have completed physics design as well as mechanical design of a novel non-intercepting diagnostic system based on a Thomson laser scattering. This diagnostic is intended for beam measurements with a CW electron beam. It is intended for a transverse beam profile measurements with sub picosecond time resolution, and for longitudinal phase space measurements as well. Working towards first experimental demonstration of such system, we have identified an appropriate laser system, which was purchased, installed and commissioned at the facility where the demonstration will take place. The main direction of our effort on transverse beam profile measurements is beam imaging i.e. 2D transverse beam profile measurements. Diffraction is the main challenges for large dynamic range imaging. Working on this problem we have implemented a new numerical code for simulation of optical field propagation. It is based on quasi-discrete Hankel transform. Its advantage over other codes is that it allows simulations of systems with significantly larger aperture and requires a significantly smaller amount of computer memory. In turn this allows us to complete such calculations without a supercomputer. We have used the code to design an amplitude apodized imaging system where diffraction effects are reduced by several orders of magnitude. Then we have manufactured and bench tested such amplitude apodized optical system experimentally demonstrating significant reduction of the diffraction effects, although not quite as strong as simulations were predicting, which requires further studies. We are also working on an alternative to the beam imaging transverse beam profile measurements technique, which does not require an optical system and therefore is not affected by diffraction. This technique is an improvement of existing wire-scanner diagnostic.

EARLY CAREER: High Repetition Rate Ultra-Fast Electron Diffraction Development

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Sr. Investigator(s):
Students: 0 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding: \$500,000 (2014)

PROGRAM SCOPE

Ultrafast phenomena have been one of the main research topics during the last decade. Thanks to the combination of ultra-fast pulses and pump-probe techniques, the observation of transient effects with atomic resolution is becoming a reality. Scientists are pursuing the dream of molecular and atomic movies that will clarify the connections between the structure and the function of biological systems, and enhance our understanding of chemical and biochemical reactions, following transformation pathways. We are pursuing the use of the Advanced Photocathode Experiment (APEX) photo-gun as novel source for time-resolved electron diffraction studies. The electron source has been designed, built and successfully tested at LBNL. It combines, unique in its genre, the high accelerating field needed for bright beams, MeV electron energy essential for time resolution in gas-phase experiments and studies of bulk processes, together with continuous (CW) operations. Ultra-short electron pulses can be delivered with a maximum repetition rate of around 186 MHz at the sample, enabling new science and

new experimental techniques. As an example, structural transitions of complex isolated molecules in gas phase could be imaged with sup-picosecond time resolution.

FY 2014 HIGHLIGHTS

This research program started July 1, 2015. In these first months, most of the effort was directed to the study and design of a beamline optimized for ultrafast electron diffraction experiments, delivering high brightness beams with a large parameter space to the sample chamber. Aberrations, space charge, and electron-electron scattering have been taken into account in simulating the results by using many different codes. The flexibility in time duration and energy spread was ensured by the use of A CW rf-buncher after the electron gun and by a low energy achromatic dog-leg. Beam compression down to 100 femtoseconds has been simulated, with 1 million particles per bunch, and down to 25 femtoseconds with collimating 70% of the charge. The beamline has been designed and the hardware is on order. Installation up to the sample chamber is expected to start in early spring 2015. Work on the laser system has started, stabilizing in time, energy and pointing, taking advantage of the high repetition rate for suppressing the noise up to high frequencies. The pointing jitter at the cathode was decreased down to 5 microns root mean square, and work on the time jitter is ongoing.

Demonstration of the Viability of SCU Technology for an FEL-Type Undulator

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Students:	0 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	\$200,000 (2014)

PROGRAM SCOPE

This project is part of a larger scope project, in collaboration with SLAC, ANL, and LBNL, to demonstrate the viability of superconducting undulator (SCU) technology for FELs, by building, measuring, testing, and correcting two 1.5-m long prototype SCU's using two different technologies. The first technology is based on conductors of NbTi, the chosen technology at ANL, and the second is Nb₃Sn, the choice at LBNL. The specific scope of work is to design and oversee the integration of a universal magnetic mounting system that allows two completely different superconducting magnets to be consecutively tested in a single, multipurpose cryostat. The funding is utilized for engineering and physics support during the development period. The ANL deliverable is the design of the universal mounting system and vacuum chamber that allows two different undulator magnets to be consecutively installed and tested in the ANL-designed cryostat that houses the entire SCU. ANL engineers and physicists optimized the design of the existing cryostat and cold mass to add the flexibility of accommodation of various types of undulatory and beam vacuum systems.

FY 2014 HIGHLIGHTS

A universal magnetic mounting system has been designed and is currently under fabrication to support the LCLS SCU Project. The system will support the operation, testing, measurement, and tuning of two distinct SCU magnets: a NbTi-based magnet fabricated by the ANL, and a Nb₃Sn-based magnet built by the LBNL. The system is an extension of proven SCU technology at ANL and is compatible with an

existing cryocooler-based SCU cryostat design. The magnetic mounting system has been further modularized to allow independent fabrication and assembly of two completely different superconducting magnet prototypes on separate, interchangeable 'cold mass' frame systems. These systems can be quickly exchanged following a magnet test with minimal disturbance to the cryostat itself. Building two separate and independent frame systems permits parallel fabrication and assembly of each magnet design. Each system supports the specific needs of the magnet, including cooling connections, beam vacuum chamber systems, current leads, tuning/shimming systems, and support/alignment systems. The systems share common suspension points to the overall cryostat and are designed for maximum heat loads that do not exceed the available cooling power of the cryostat. The beam vacuum chamber for each frame system is based on a common extrusion profile but is tailored to the magnet. This provides compatibility with particular features of each magnet design while preserving identical thermal transition interface points at the cryostat ends.

EARLY CAREER: High Performance Toolkit for Photon Science

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Students: 2 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding: \$500,000 (2014)

PROGRAM SCOPE

Light sources are Basic Energy Science facilities that serve thousands of researchers per year. These facilities are currently generating scientific data faster than can be analyzed using the computational methods of the past, so that scientific discovery is limited by the inability to rapidly analyze large data sets. The high performance toolkit will accelerate the rate of scientific discovery by enhancing the rate at which data can be analyzed. The main focus will be to develop and expand tools for analyzing large volumes of light source data. All tools in the toolkit will be optimized for parallelization on multiple central processing units (CPU), graphical processor units (GPU), and hybrid CPU/GPU multicore architectures. This will decrease analysis times by several orders of magnitude while simultaneously permitting larger data sets to be processed. The initial focus will be in the development of tools for scattering, in particular for grazing incidence small angle X-ray scattering and small angle X-ray scattering. An easy-to-use graphical user interface will be developed for the toolkit that can be easily accessed by a broad scientific audience.

FY 2014 HIGHLIGHTS

The main focus over last year has been the development of the toolkit for real-time applications at a synchrotron. Currently, scientists visiting synchrotrons most commonly copy their collected data onto portable hard drives, only to look at the data in detail after their time has already ended. The scientists have no means of adjusting or evaluating the experiment during the beamtime. However, creating instant feedback will supply the experimenter with knowledge to adjust their experiments and hence optimize the beamtime without having to wait usually several months for the next beamtime. In order to move into this regime, our developments over the last year focused on new and high performance algorithms to fit small angle X-ray scattering and grazing incidence small angle X-ray scattering data. These developments are now part of the "Center for Applied Mathematics for Energy Research

Applications: CAMERA.” The new developments were demonstrated as part of a larger effort to illustrate the concept of a “super facility” and evaluate the current state of the art for real-time analysis. The concept of a Super Facility is the seamless integration of multiple, complementary DOE Office of Science User Facilities into a virtual facility that presents a fundamentally greater capability for users. The multiple DOE User Facilities involved in the Demonstration were ALS (BES), NERSC (ASCR), OLCF (ASCR), ESnet (ASCR) and several other efforts: Globus Online (ANL) and SPOT (LBNL-CRD). We illustrated the ability for researchers, doing time-resolved work at a scattering beamline, to see near real-time analysis of their samples, running a large scale simulation on Titan at OLCF orchestrated and presented, without user interaction, using SPOT. Thus, enabling researchers, for the first time, to understand their samples sufficiently during beamtime and to adjust the experiment to maximize their scientific results.

Superconducting Spectrometers for Next Generation Light Sources: Making Every Photon Count

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Funding: \$832,400 (2014)

PROGRAM SCOPE

SLAC, ANL, and NIST are developing superconducting x-ray spectrometers for DOE light source applications. The higher efficiency provided by the Transition-Edge Sensors (TES) x-ray spectrometers will enable important new science at both free-electron and synchrotron facilities. Superconducting spectrometers can increase the solid angle by more than two orders of magnitude over gratings, providing new capabilities to measure metals with L emissions in the soft x-ray regime, including Ti, V, Cr, Mn, Fe, Co, Ni, and Cu, which are critical components to systems as diverse as the Photosystem II part of the photosynthetic pathway and advanced magnetic-information storage devices. This new capability will broadly impact x-ray emission and x-ray absorption spectroscopy in the soft-, tender-, and hard x-ray regimes. Scanning-nanoprobe-imaging beamlines will also benefit greatly from superconducting spectrometer arrays, resolving essentially all elemental x-ray fluorescence overlaps and also provide a wealth of chemical detail in x-ray emission spectra in acquisition times much smaller than previous instrumentation. The US leads the world in the development of superconducting x-ray spectrometers. Capitalizing on this lead enables unique capabilities and instrumentation that will provide a competitive advantage for US light sources. This program unleashes the true potential of this technology at the next generation of free-electron laser facilities and in synchrotron light sources.

FY 2014 HIGHLIGHTS

While this is a new program that has just begun, significant progress has already occurred. During the first few months of this work, we have (1) Designed soft x-ray pixels with a higher response time. We are proceeding to fabricate and test them. If successful, these pixels will be a significant step towards operating superconducting spectrometers on next generation free-electron light sources with higher anticipated frame rates. (2) For the first time, we have designed, fabricated, and tested microwave SQUID multiplexer chips with a much higher per-pixel bandwidth than previously achieved. This accomplishment is a significant step towards larger and faster superconducting spectrometer arrays for

both FEL and synchrotron facilities. (3) We have initiated a study of a comprehensive range of science experiments at both LCLS-II and the APS. This study will establish performance metrics for superconducting spectrometer instruments to study a wide range of high-impact science problems at both facilities.

Oscillator-Type X-Ray Free Electron Laser to Realize the Full Potential of X-Ray Lasers for Materials Sciences and Fundamental Physics

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Funding: \$400,000 (2014)

PROGRAM SCOPE

The X-ray free-electron laser oscillator (XFEL) is a device that combines the brightness of an FEL with the stability of a storage ring and the energy bandwidth of a high-resolution monochromator. The fully coherent, ultra-high spectral purity of hard x-ray pulses from an XFEL will drastically expand the reach of techniques developed at third-generation sources, offering the prospect of solving problems such as the physics of high T_c superconductivity. The XFELs and high-gain amplifiers will complement each other—together they will realize the fullest potential of FEL-based photon sciences. If an XFEL operates at one of the higher harmonic frequencies, the electron energy need not be very high, and one can significantly reduce the construction and operating costs of the CW superconducting accelerator. Thus, XFEL operation appears to be feasible at the future LCLS-II facility with the planned 4 GeV CW superconducting Radio-Frequency (RF) linac and a part of the Hard X-ray (HXR) undulator. Furthermore, the successive XFEL pulses can in principle be phase-locked to each other by stabilizing the cavity roundtrip time to within a small fraction of the wavelength, by referencing the output to an absolute external reference, such as the narrow nuclear resonance line of ^{57}Fe . A mode-locked XFEL with its x-ray spectral comb can serve as a powerful new tool for x-ray metrology and fundamental physics. The R&D goal of this proposal are: to establish the tolerance limits for errors and jitters, to assess the possibility of operating a harmonic XFEL at the LCLS-II in collaboration with SLAC National Accelerator lab scientists, to perform a feasibility study of inter-pulse mode-locking of XFEL for x-ray spectral comb generation, and to complete an experimental study of radiation damage issues of diamond crystals which serve as the near-normal incidence reflectors of the x-ray cavity. We plan to hold a two-day workshop exploring the scientific opportunities offered by an XFEL.

FY 2014 HIGHLIGHTS

(1) Progress in diamond crystal durability test: A beam time is allocated at the APS 34 ID-E for 2015-1 run to irradiate a diamond sample with the insertion device (ID) beam focused to 0.5 micron spot size generating power density comparable to the XFEL environment. The sample chamber is being constructed. A postdoc offer is in progress to work on the diamond durability experiment. (2) In collaboration with the SLAC LCLS group: A concrete scheme of an XFEL at ESA (End Station A) building was considered. A zigzag optical cavity will fit in this building either with 2 MHz operation of the accelerator, or with 1 MHz operation. Be-CRLs (compound refractive lenses), rather than the large and heavy K-T mirrors, are determined to be a low loss, compact option as the focusing elements. The

spectral flux in meV from an XFEL at LCLS II will be three orders of magnitudes higher than that can be obtained by nonlinear harmonic generation of high-gain operation of LCLS II assuming a superconducting undulator for the latter. Scientifically, an XFEL at LCLS II could provide unique tools to address the question of the underlying physics of the emergent phenomena in strongly correlated electron systems with the obvious example: high T_c superconductivity. This will be an essential extension of the LCLS II capability.

EARLY CAREER: High Resolution Spectroscopic X-ray Detectors using Superconducting Sensors

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Funding: \$2,500,000 (2010-2014)

PROGRAM SCOPE

This detector R&D program intends to develop the next-generation of energy dispersive detectors using superconducting technology. Currently, we are focusing on developing a superconducting technology called microwave kinetic inductance detectors (MKIDs), which is a resonator-based technology. This detector R&D is targeted for high resolution x-ray spectroscopic applications, such as x-ray emission and absorption spectroscopy, but also has the potential to impact techniques such as Compton scattering and energy-dispersive diffraction at high energies. The overall goal is to develop broadband energy-dispersive detectors with energy resolutions < 5 eV at 10 keV with count rates comparable to silicon drift diodes. For example, this detector could make possible x-ray emission spectroscopy at scanning nanoprobe. For superconducting detectors, the ability to multiplex is crucial to reach high count rates and large solid-angles (i.e., many pixels). MKIDs can be multiplexed in a straightforward manner and can reach pixel counts of about 10,000. An Early Career Award (4/2010 - 4/2015) has made this R&D possible. The goal of the Early Career Award is to determine whether or not MKIDs themselves can be used as the sensor or whether it is better to couple MKIDs to another technology (e.g., resonator readout SQUID/TES arrays) in collaboration with other groups.

FY 2014 HIGHLIGHTS

We have published a paper using kinetic inductance detectors in quasi-thermal equilibrium. However, improvements in the noise performance are necessary. To this end, we have developed a fabrication process to etch sloped sidewalls in silicon nitride in order to grow the capacitor on bare silicon. The multiple pixel readout using the Robotic Autonomous Crawling Hexapod (RoACH) electronics continues with firmware development to allow using Fast Fourier Transforms (FFTs) to sweep the resonator and firmware for pulse thresholding the data. We are able to acquire triggered pulse data from up to 256 resonators. We are developing a new method of pulse processing using a multivariate analysis which assumes no prior knowledge of the data. In particular, we use principal component analysis (PCA) to reduce and noise-filter the data, followed by cluster analysis to classify similar pulses. PCA provides an orthogonalized, decomposed representation of the data by their degree of covariance and thus significance. By selecting the first few components according to their degree of covariance, and

rebuilding the data matrix, main features remain and noise is filtered. PCA is a non-parametric analysis which is in contrast to more traditional pulse processing methods (e.g., optimal filters), which are parametric methods and assume some prior knowledge of the dataset (e.g., known signal shape). These parametric methods maximize the signal to noise under the conditions that the pulse shape and noise are stationary, and the pulse shape is linear. However in real detectors, these conditions are not always satisfied. Our goal is to improve on the optimal filter with a PCA-based method. This method is applied to a simulated data set as well as a data set from an x-ray thermal kinetic inductance detector and an x-ray TES detector. We demonstrated that the PCA is able to fit pulses with severe position dependence. We continue to develop this method in order to treat data which have variable pulse shapes with energy (i.e., non-linear pulses).

EARLY CAREER: Inorganic Nanocomposite Electrodes for Electrochemical Energy Storage and Energy Conservation

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Funding: \$2,500,000 (2010-2014)

PROGRAM SCOPE

Dr. Milliron proposes to develop a combinatorial approach to solution-processed inorganic nanocomposite materials as a new route to the complex physical properties required for efficient energy storage and conservation devices. Inorganic nanocomposites have recently emerged as a means of controlling the properties of electronic materials through morphology as well as composition to give rise to combinations of properties not generally found in homogeneous, single-phase materials. For example, electrodes for batteries and electrochromic window coatings must efficiently conduct both electrons and ions to achieve high power and efficient coloration, respectively. The Milliron group has recently demonstrated a new method for preparing inorganic nanocomposites from solution-processible colloidal nanoparticle and molecular building blocks in a combinatorial manner. Here, we propose to apply this general approach to the fabrication of well-controlled, chemically and morphologically tunable inorganic nanocomposites for electrochemical energy applications. First, silver chalcogenide nanoparticles are investigated as model mixed ionic and electronic conductors. These are embedded in a semiconducting matrix and the interfacial area is systematically varied to reveal the contribution of interfaces to the overall ionic and electronic transport behavior. These properties suggest design rules to guide the development of highly efficient mixed conductors for energy applications. Going beyond transport, this nanocomposite platform will be further developed to resolve fundamental questions in order to guide the development of advanced battery and electrochromic device electrodes. Nanocomposite battery electrodes will be fabricated and electrochemically characterized in an effort to uncover the source of rapid degradation in charge capacity which currently limits practical application of ultrahigh energy density conversion materials, such as tin and germanium compounds.

FY 2014 HIGHLIGHTS

8 peer-reviewed publications were supported in part by this grant during FY14: [1] JB Rivest, G Li, ID Sharp, JB Neaton, DJ Milliron*, "Phosphonic Acid Adsorbates Tune the Surface Potential of TiO₂ in Gas and Liquid Environment," J. Phys. Chem. Lett. 5 (2014), 2450-2454. <http://pubs.acs.org/doi/abs/10.1021/jz501050f> [2] EL Runnerstrom, A Llordes, SD Lounis, DJ Milliron*, "Nanostructured electrochromic smart windows: Traditional materials and NIR-selective plasmonic nanocrystals," Chem. Commun. 50 (2014), 10555-10572. (invited Feature) <http://xlink.rsc.org/?doi=C4CC03109A><http://pubs.rsc.org/en/content/articlehtml/2014/cc/c4cc03109a> [3] SD Lounis, EL Runnerstrom, A Bergerud, D Nordlund, DJ Milliron*, "Influence of dopant distribution on the plasmonic properties of indium tin oxide nanocrystals," J. Am. Chem. Soc. 136 (2014), 7110. <http://pubs.acs.org/doi/abs/10.1021/ja502541z> [4] SD Lounis, EL Runnerstrom, A Llordes, DJ Milliron*, "Defect chemistry and plasmon physics of colloidal metal oxide nanocrystals," J. Phys. Chem. Lett. 5 (2014), 1564. (invited Perspective) <http://pubs.acs.org/doi/abs/10.1021/jz500440e> [5] EL Rosen, AM Sawvel, DJ Milliron, BA Helms*, 'Influence of surface composition on electronic transport through naked nanocrystal networks,' Chem. Mater. 26 (2014), 2214. <http://pubs.acs.org/doi/abs/10.1021/cm404149u> [6] TM Mattox, A Bergerud, A Agrawal, DJ Milliron*, "Influence of shape on the surface plasmon resonance of tungsten bronze nanocrystals," Chem. Mater. 26 (2014), 1779. <http://pubs.acs.org/doi/pdf/10.1021/cm4030638> [7] DJ Milliron*, R Buonsanti, A Llordes, BA Helms, "Constructing functional mesostructured materials from colloidal nanocrystal building blocks," Acc. Chem. Res. 47 (2014), 236. <http://pubs.acs.org/doi/pdf/10.1021/ar400133k> [8] A Dong*, Y Jiao, DJ Milliron, "Electronically coupled nanocrystal superlattice films by *in situ* ligand exchange at the liquid-air interface," ACS Nano 7 (2013), 10978. <http://pubs.acs.org/doi/pdf/10.1021/nn404566b>

Accelerator R&D for a Soft X-Ray FEL: Echo-Enhanced Harmonic Generation

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Funding: \$1,000,000 (2014)

PROGRAM SCOPE

The Echo Enabled Harmonic Generation (EEHG) technique is a promising approach for external seeding of a soft x-ray Free Electron Laser. External seeding offers the promise of x-ray pulse shaping and control analogous to that demonstrated with optical lasers. The EEHG technique relies on beam manipulation rather than laser manipulation to up-shift the frequency of the external seed which should provide more stable and easily controlled output pulses. EEHG has been demonstrated at harmonic numbers as high as 7. This program will study the EEHG approach at harmonic numbers as high as 75 in a phased approach to gain maximal understanding to the technique and the fundamental physics. In parallel, this program will study approaches to generating the necessary external laser seed which must have excellent control of the laser spectral phase and the laser wavefront. The benefit will be a much better understanding of the external seeding approaches and, if successful, these two elements could be combined in a facility to provide an external seed of <3 nm.

FY 2014 HIGHLIGHTS

In FY14, the program made a very clear comparison between the EEHG (Echo) and High-Gain Harmonic Generation approaches at the 15th harmonic showing the improved beam and radiation stability that Echo will achieve. The program then began the upgrade program to reach higher harmonics. Along these lines, the VISA undulator segment was shipped from Brookhaven National Laboratory, refurbished at SLAC, and then installed in the NLCTA tunnel. Commissioning of the VISA undulator will begin in early FY15 and measurements of the 30th and 75th harmonics will be made in mid- and then late FY15, respectively.

EARLY CAREER: Combining Scanning Probe Microscopy and Synchrotron Radiation for Nanoscale Imaging with Chemical, Electronic and Magnetic Contrast

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Funding: \$500,000 (2014)

PROGRAM SCOPE

The objective of this research is to develop a novel high-resolution microscopy technique, synchrotron x-ray scanning tunneling microscopy (SX-STM), for imaging of nanoscale materials with chemical, electronic, and magnetic contrast. SX-STM will combine the sub-nanometer spatial resolution of scanning probe microscopy with the chemical, electronic, and magnetic sensitivity of synchrotron radiation. The development will drastically increase the spatial resolution of current state-of-the-art x-ray microscopy from only tens of nanometers down to atomic resolution. The technique will enable fundamentally new methods of characterization, which will be applied to the study of energy materials, nanoscale magnetic systems, and site-specific heterogeneous catalysis. A better understanding of these phenomena at the nanoscale has great potential to improve the conversion efficiency of quantum energy devices, lead to advances in future data storage applications, and yield more efficient catalytic reactions.

FY 2014 HIGHLIGHTS

Using our novel and patented topo filter as well as new method to fabricate specialized smart tips we have achieved record-breaking elemental contrast of Ni islands on a Cu substrate at the ultimate limit of single atomic height and a lateral spatial resolution of 2 nm. We were able to conclude that electron tunneling causes the high spatial resolution and not photoejection as previously believed. The topo filter allows separating topographic information from chemical and magnetic data that are otherwise convoluted in the SX-STM signal. In this way we have achieved stable tunneling conditions even during high brilliance x-ray radiation of the sample. Further, we have used molecular beam epitaxy and focused ion beam milling to fabricate metal-insulator-metal smart tips that focus signal detection to the apex and provide therewith highly localized information. We have successfully extended the materials that can be used for smart tip fabrication, starting from Pt-Ir to W, Fe, and Gd. Methods for the growth of insulator-metal films with painted contacts have been developed. In order to enable measurements at photon energies in which air absorption would become restrictive we have developed and built a

custom high-speed ultra-high vacuum compatible optical beam chopper. It delivers a modulated tip and sample current that is used for lock-in analysis. A custom ultra-stiff x-y-z-r manipulator equipped with LHe flow cryostat was developed. It provides cooling capabilities for a new microscope that we have built. It will be the world's first low-temperature SX-STM. We have built a vacuum suitcase to transfer samples between the microscopy chamber and a separate preparation chamber in order to maximize actual measurement time at the synchrotron. An *in situ* nanopositioning system with 5 degrees of freedom was designed. It enables alignment of a focusing x-ray capillary or zone plate. The focusing element drastically enhances the flux density for SX-STM experiments.

High Repetition Rate Photoinjector

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Funding: \$3,494,000 (2014)

PROGRAM SCOPE

The project 'High Repetition Rate Photoinjector' (a.k.a. Advanced Photo-injector EXperiment or APEX) at the Lawrence Berkeley National Laboratory is dedicated to the development of a new concept high repetition rate high-brightness electron source for free electron laser applications. The successful development of such source will critically impact the performance of future 4th generation light sources when MHz-class repetition rates are required. The core of the system is the Very High-Frequency (VHF)-Gun, a normal-conducting continuous wave (CW) RF gun where electrons are generated by laser-induced photo-emission on high quantum efficiency (QE) cathodes and accelerated up to an energy of 750 keV. The gun cavity resonates at 186 MHz, the 7th sub-harmonic of 1.3 GHz. The low frequency makes the resonator size large enough to lower the power density on the cavity walls at a level that conventional cooling techniques can be used to run in CW mode. A second advantage of the low frequency is the long wavelength that allows for large apertures on the cavity walls with negligible field distortion. Such apertures provide the vacuum conductance necessary to achieve the low pressures required to operate the sensitive QE cathodes with acceptable lifetime. A last advantage of such a scheme is that it is based on mature and reliable RF and mechanical technology, an important characteristic to achieve the reliability required to operate in a user facility. The APEX project was initiated at the end of 2009 to develop over 6 years the VHF-gun and test its capability of operating in an injector delivering the necessary performance. APEX is organized in 3 stages (Phase 0, I and II), with the first 2 dedicated to the development and testing of the gun, cathode testing and electron beam characterization at the gun energy. In Phase II, a linac is added to the VHF-Gun to accelerate the beam up to 30 MeV reducing space charge forces to perform a reliable characterization of the gun brightness performance.

FY 2014 HIGHLIGHTS

(1) Tests of the high QE cesium telluride cathodes were completed and requirements were satisfied by large margin. The cathodes were tested at 1 MHz repetition rate with charges per bunches ranging from few tens of pC to beyond 300 pC. QE and QE lifetime were measured over many days at the nominal gun power. Minimal requirements for those quantities (based on LCLS-II needs) were demonstrated by a

large margin. In general, QEs above 10% and QE lifetime of more than 30 days were measured. Such results represent the successful demonstration of one of the main milestones of the APEX program. (2) In high repetition rate FEL and ERL applications, containing the level of dark current emitted by the gun is fundamental to avoid radiation damage of downstream accelerator components and/or quenching of superconducting RF structures. Dark current was characterized at APEX and the results showed a figure (350nA) that already meets the LCLS-II requirements of less than 400 nA. The tests also allowed defining a multistep strategy to further reduce dark current. A paper reporting such results has been recently accepted for publication on Phys. Rev. Special Topics, Accel. and Beams. (3) Phase-I beamline with its diagnostic system for the 6D characterization of the beam phase space was completely installed. Phase-I commissioning initiated in June 2014 but was interrupted in August due to a failure in one of the coaxial lines that feed the power to the gun. The event caused the rupture of a RF window and the gun contamination. The recovery from the failure is now being completed and the beam tests will restart after the RF conditioning of the cavity. (4) Phase II activity achievements included, finalizing the design of the RF distribution network and of the buncher, initiating the fabrication of the linac accelerating sections, performing most of the acceptance test of the RF system that feeds the power to the linac and to the deflecting cavity, assigning the bid for the buncher RF source.

Advanced Photon Detector Development for Synchrotron Radiation Applications

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Funding: \$600,000 (2014)

PROGRAM SCOPE

The project conducts research and development of advanced x-ray detectors for synchrotron radiation applications. It includes custom detectors for x-ray correlation spectroscopy experiments and for high-energy x-ray diffraction.

FY 2014 HIGHLIGHTS

Successful demonstration of the first 3D-integrated x-ray detector and its application to x-ray correlation spectroscopy experiments. Capture of events at a 153 ns resolution was demonstrated, and correlation measurements to well below 1 ms (limited only by the available beam intensity) were made. A new 64-element germanium detector was fabricated and integrated with BNL-designed application specific integrated circuits (ASICs) to form a 1D position-sensitive spectroscopic detector ideally suited to time- and position-dependent structural changes, for example in an operating battery.

Photocathodes for High Repetition Rate Light Sources

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Funding: \$621,500 (2014)

PROGRAM SCOPE

The focus of this program is on photocathodes for high repetition rate Free Electron Lasers (FELs) and Energy Recovery Linacs (ERLs), including testing in a variety of photoguns. Teams from BNL and LBNL lead this work, which involves collaborators from ANL and Helmholtz Zentrum Berlin (HZB). This work follows on from a successful previous project that developed and applied the tools of modern materials science to understand and optimize cathode performance. The program is concentrated in three areas: a) Physics and chemistry of alkali-antimonide cathodes (BNL – LBNL) b) Development and testing of a diamond amplifier for photocathodes (BNL) c) Tests of both cathodes in copper RF photoguns (LBNL)

FY 2014 HIGHLIGHTS

For most of 2014, our focus has been on optimizing Alkali antimonide cathodes to produce smoother surfaces. Our previous work had demonstrated that these cathodes have a significant roughness (25 nm RMS roughness, with a 100 nm spatial period, for a 50 nm thick film), even when grown on an atomically smooth surface. Our previous work also demonstrated a correlation between the applied electric field and the emittance of the electrons emitted from the cathode (this measurement was made with a custom device that was invented at LBNL as part of this work). The observed roughness explains this correlation; this in turn suggests that the growth process must be modified to achieve cathodes with less roughness, while still maintaining high quantum efficiency. We have identified the source of this roughness to be the dissolution and recrystallization of the crystalline antimony precursor layer upon deposition of potassium. We have varied our deposition process to avoid the production of crystalline antimony - instead using a multilayered approach. This produced a cathode with 60% of the ideal Quantum Efficiency (QE), but almost an order of magnitude (3.3 nm vs 25 nm) reduction in roughness. This development will continue in 2015 to explore both co-deposited films and sputtered film - the production of a viable sputter target for this material was another significant accomplishment of this program in 2014.

Ultrafast Science Enabled by Femtosecond MeV Electron Diffraction

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Funding: \$574,000 (2014)

PROGRAM SCOPE

SLAC is working on an Ultrafast Electron Diffraction (UED) R&D program with the goal of providing MeV-, 100-femtosecond-scale electron pulses to support an ultrafast science program. The UED R&D will be carried out using the existing infrastructure at the ASTA accelerator test bunker at SLAC. It will be the first UED implementation to break the 100-fs time resolution barrier, and it will have an order of magnitude higher repetition rate (120 Hz vs. 10 Hz) than other existing UED implementations. The first experimental results are expected in early September 2014.

FY 2014 HIGHLIGHTS

ASTA UED was successfully commissioned in early September of 2014. Single-shot diffraction patterns were obtained for Au and Bi films. This is the first step towards establishing sub-100 fs ultrafast electron diffraction for probing the nuclear motion in photo-chemistry and materials science.

EARLY CAREER: Visualizing and Controlling Energy Excitation and Transport in Mesoscale Organic and Inorganic Material Composites

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Funding: \$500,000 (2014)

PROGRAM SCOPE

Energy is created in matter from light via quantum excitations: electron excitations, phonons, bound electron-hole pairs (excitons), and collective excitations (plasmons). Since the advent of quantum mechanics these 'creation' processes have been studied and are relatively well understood. To utilize the energy however we need to understand how this energy can be propagated from its point of origin, at the molecular level, to mesoscopic, microscopic and macroscopic distances, where it can be harnessed. It is the study of these transport processes that are at the core of this proposal.

Harnessing and deliberately directing energy created by material excitations is yet to be demonstrated at meaningful length scales for energy device architectures. Of specific interest are excitons that constitute the core of light-matter interactions and mediate all opto-electronic conversion processes in nano building units, such as molecules or nano crystals. Understanding and controlling the exciton transport through nano building block assemblies has profound implications on light harvesting and emitting materials, the synthesis of novel mesoscale structures with specific optoelectronic functionalities, nano electronics, and photo-induced biological processes.

A unique microscopy technique has been developed in my laboratory to visualize energy transport within structured nano building block assemblies: A nano optical light source (plasmonic antennae) excites a tiny area of the nano building block assembly. In parallel a scanning probe tip scans over the sample, mapping the material response due to the local excitation. Using the combination of local excitation and local probe technique resolves exciton diffusion with sup 10 nm spatial resolution.

We plan to explore: 1) exciton diffusion length and dynamics in organic and perovskite based photovoltaic materials in dependence of their local morphology (e.g crystallinity); and 2) measure the spatial extend of exciton transport via Foerster Resonance Energy Transfer in mono disperse and poly disperse inorganic nano building block assemblies.

FY 2014 HIGHLIGHTS

We were able to make advances on three fronts: 1. Mapping optoelectronic processes in state of the art perovskite photovoltaic materials; 2. Mapping exciton transport through CdSe quantum dot arrays and polymer thin films; 3. Manipulating excitons to engineer the currently smallest light switch. [1] In collaboration with the Joint Center for Artificial Photo syntheses we characterized high efficient perovskite PV devices (>16%) and discovered an enormous local heterogeneity between different grains

using state of the art near field optics. The most exciting finding is that these devices already include a few individual grains that operate close to the Shockley Queisser limit (32%). This insight will lead to a systematic and fast optimization process of this material class. [2] Using the techniques proposed in the proposal we were able to find an exciton diffusion length in CdSe Quantum dots of >100nm and determine how to manipulate the diffusion length which is the base for the potential development of novel PV light absorbers. For the most popular organic P3HT polymer materials we determined a diffusion length of 20nm and more importantly that the diffusion length can be manipulated via strong field gradients. The latter result might open up the approach for exciton transport manipulation and lead to novel approaches in information technology. [3] We demonstrated how to manipulate Förster Resonance Energy Transfer mediated energy transfer between individual PbSe Quantum Dots and gated layers of graphene. The main outcome is that the luminescence can be turned on and off from individual quantum dots with enormous speeds taking advantage of the high mobility of graphene and in ambient conditions. This is extremely interesting for miniaturizing light modulators for the information industry, where the smallest light modulators are currently tens of micrometers large and are reduced here to individual 4 nm quantum dots (Nano Lett., 2014, 14 (12), pp 7115–7119).

EARLY CAREER: Generation of Coherent Stable Terawatt-level Hard X-Ray Free Electron Laser Pulses with Femtosecond Duration

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Funding: \$500,000 (2014)

PROGRAM SCOPE

Terawatt (TW) peak power Free Electron Laser (FEL) can enable the single molecule imaging and study of nanometer or even finer structure. The goal of this project is to study the feasibility to generate tunable, fully coherent TW peak power hard x-ray FEL pulses with more than $1.0E+13$ photons/pulse in 10 femtoseconds duration. This will be more than one-order of magnitude higher peak power than existing hard x-ray FEL facilities like LINAC Coherent Light Source (LCLS) provide. A promising way to generate such high power FEL pulses is to amplify a coherent seed through a highly tapered undulator. The seed must be predominantly coherent with stable intensity and a large signal-to-noise ratio. We propose an improved Self-Amplified Spontaneous Emission (iSASE) scheme to generate such a seed [1, 2]. Other seeding schemes, such as self-seeding, are also studied and compared to iSASE. Self-seeding has been demonstrated at LCLS, which not only proved the reduction of frequency bandwidth, but also requests further improvements to increase the taper efficiency. Approaches to overcome these challenges will be studied. For an iSASE, phase shifters are interlaced between undulators sections to mix the phase and amplitude of the FEL radiation coherent spikes. This increases the cooperation length, and gradually narrows the spectrum of the FEL. With such an iSASE scheme, a coherent seed, with stable intensity and large signal-to-noise ratio, can then be efficiently and stably amplified to TW-level in a highly tapered undulator. Such an iSASE seed is intrinsically tunable, much like SASE, in contrast to other seeding schemes which tend to have limited tuning range. This project aims at a thorough study to generate tunable, fully coherent stable TW-level hard x-ray pulses having a few femtoseconds duration, both in theory and experimentation. [1] J. Wu, A. Marinelli, and C. Pellegrini, Proc. FEL2012, p. 237, Nara, Japan. [2] J. Wu *et al.*, Proc. IPAC2013, p. 2068, Shanghai, China.

FY 2014 HIGHLIGHTS

(1) In an iSASE FEL, undulator sections are interlaced with phase shifters. To systematically study and optimize iSASE, a simulation package was developed in April, 2014. Since an iSASE seed starts from the random shot noise in the electron bunch, a statistic analysis is necessary. The iSASE scheme is studied with 1000 simulation sets, which are generated with a random start from shot noise, and also include random phase shifter error. The results enabled us to observe the statistic nature, and quantify the statistical fluctuation of the iSASE seed power and bandwidth. (2) The critical add-on for an iSASE FEL is to introduce phase shifters and interlace them with undulator sections to enhance the slippage between the FEL and the electron bunch. To connect my Early Career Research Project to SLAC's most important project LCLS-II, based on the LCLS-II base line, phase shifters are designed to show that an iSASE can be configured for LCLS-II. (3) For a tapered FEL, the power can increase by a factor of 100; we ask whether the FEL still has a high transverse coherence. A study on the mode content was carried out and the analysis revealed that the fundamental Gaussian mode contributes more than 95% of the total power even in the deep tapered region. This ensures that a deeply tapered FEL is highly coherent. (4) To benchmark our theoretical finding and numerical simulation result, we study tapered FEL experimentally on LCLS, both for SASE and Self-seeding FEL. Tapered FEL optimization is an intrinsically difficult task. An on-line optimization for a tapered FEL was implemented. For both SASE and Self-seeding FEL, the on-line optimizer successfully brought a random started LCLS to the optimized configuration within 20 minutes. Journal papers: [1] Phys. Rev. ST Accel. Beams 17, 110703 (2014); [2] Phys. Rev. ST Accel. Beams 17, 110701 (2014); [3] Nature Communications 5, Article number: 3762 (2014); [4] Optics Express 21, 32013 (2013); 5. Nucl. Instrum. Methods Phys. Res., Sect. A 726, 77 (2013).

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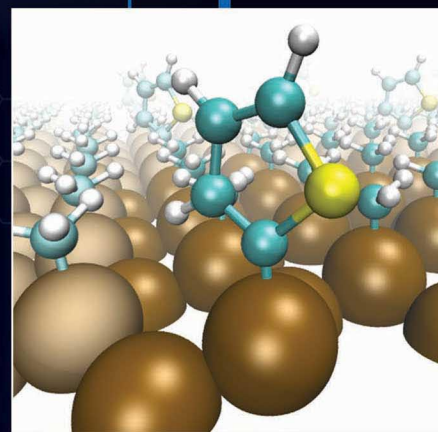
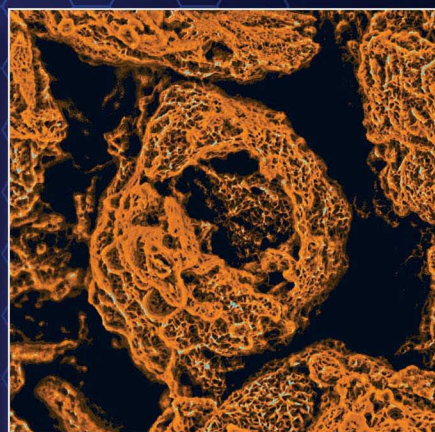
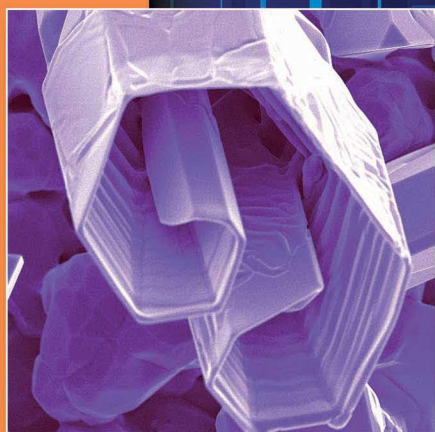
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