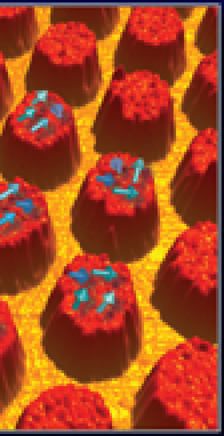

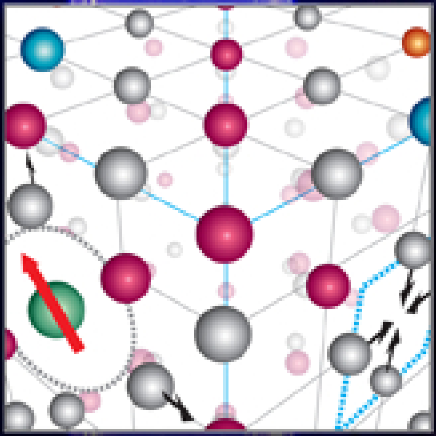

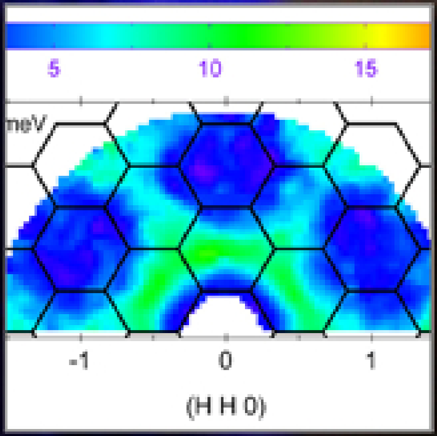

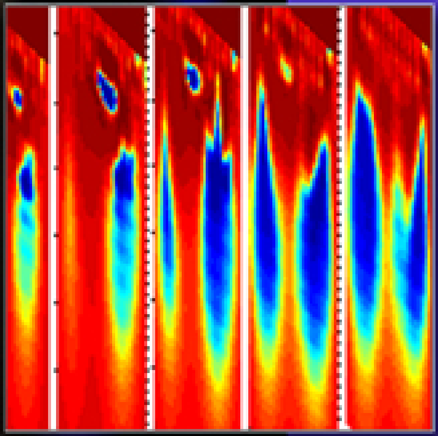

2012

Basic Energy Sciences
FY 2012 Research Summaries

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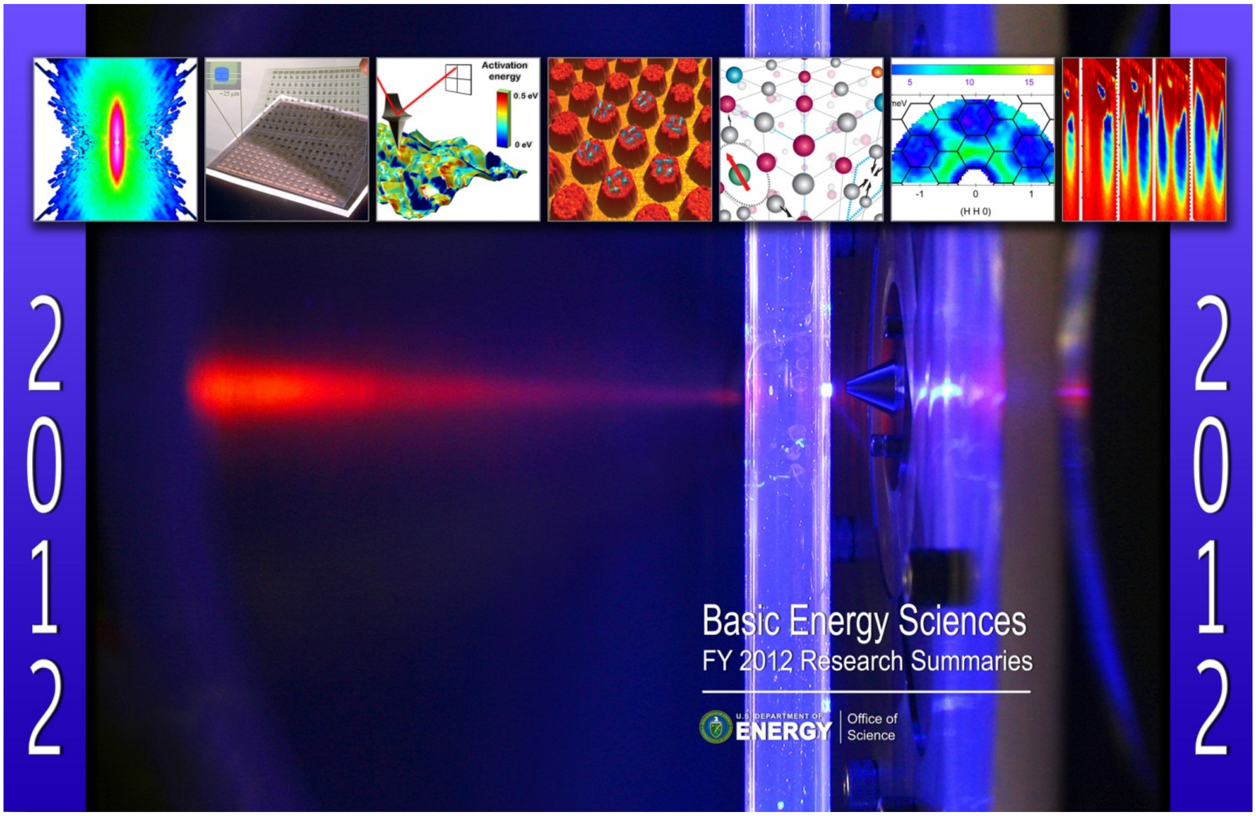

2012

Basic Energy Sciences
FY 2012 Research Summaries

U.S. DEPARTMENT OF ENERGY | Office of Science

2012

Cover Image

This photoionization/mass spectrometry apparatus at the Advanced Light Source is used to gain new insights into combustion chemistry. A unique analysis of the reaction of propene with an oxygen atom reveals the influence of electron spin on combustion chemistry.

Inset Images

Front cover, from right: (1) The ElectroMagnetic Geological Mapper (EMGeo) combines advanced geophysical imaging technologies with high-performance computing algorithms to make a powerful tool for subsurface electrical resistivity mapping, which yields new ways to discriminate underground oil and gas from surrounding geology. In the image, the blue regions contain hydrocarbon and salt and the hydrocarbon reservoir appears as a separate small, lenticular blue region above the deeper and larger salt structures. (2) This inelastic neutron scattering image of a single-crystal of the mineral $ZnCu_3(OD)_6Cl_2$ provides experimental confirmation of a new state of magnetism previously predicted by theory. This observation paves the way for a deeper understanding of high-temperature superconductivity and future applications for quantum computing. (3) This schematic representation of the atomic lattice of a tellurium-antimony-germanium-silver thermoelectric doped with rare earth dysprosium illustrates that a small addition of rare earth element can make a big difference in thermoelectric properties—the conversion of heat to electricity. (4) This atomic force microscope micrograph of arrays of niobium islands (red) on a gold underlayer (yellow) illustrate fluctuating superconducting properties of the niobium islands, which may lead to improved electronic materials with tailor-made properties and functionality.

Back cover, from right: (5) Lithium ions are caught in action in a $LiCoO_2$ thin film battery cathode in this spatially resolved activation energy map with nanometer resolution. This new microscopy fits well with macroscopic measurements and theoretical calculations and may bring revolutionary new understanding to energy storage technologies. (6) Flexible solar module that uses high performance, ultrathin compound semiconductor photovoltaic cells grown on a wafer can now be printed onto a sheet of plastic, cutting the costs of high-efficiency solar cells. (7) This electron momentum energy map of an oxygen (O_2) molecule captures the first real-time images of two atoms vibrating in a molecule. The laser-induced electron diffraction (LIED) technique offers a novel method for capturing the ultrafast motion of atoms within a molecule to better understand and control chemical reactions.

More information: http://science.energy.gov/bes/highlights/

Contents

Preface

This is a collection of summaries for more than 1400 research projects funded by the Office of Basic Energy Sciences (BES) in Fiscal Year 2012 at some 180 institutions across the U.S. This volume is organized along 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 activity. For the SUF division, summaries are provided for the research projects in accelerator physics and x-ray and neutron detectors.

This is the second 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 2012, there may be some omissions. Some specific activities are not covered, including the construction and operation of scientific user facilities, Energy Frontier Research Centers, Fuels from Sunlight Energy Innovation Hub, the Experimental Program to Stimulate Competitive Research (EPSCoR), 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 annual funding, and a brief description of the research project.

This collection is complementary to the *Basic Energy Sciences 2011 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.

Institutions Receiving Grants

Akron, University of
Alabama, University of
Alfred University
Arizona State University
Arizona, University of
Arkansas, University of
Auburn University
Boise State University
Boston College, Trustees of
Boston University
Bowling Green State University
Boyce Thompson Institute
Brandeis University
Brigham Young University
Brown University
California Institute of Technology
California State University-East Bay
California State University-Fullerton
California State University-North Ridge
California-Berkeley, University of
California-Davis, University of
California-Irvine, University of
California-LA, University of
California-Riverside, University of
California-San Diego, University of
California-Santa Barbara, University of
California-Santa Cruz, University of
Carnegie Institution of Washington
Carnegie Mellon University
Case Western Reserve University
Central Florida, University of
Central Michigan University
Chicago, University of
Cincinnati, University of
City College of New York
Clark Atlanta University
Clarkson University
Clemson University
Colorado School of Mines
Colorado State University
Colorado, University of
Columbia University
Connecticut, University of
Cornell University
Dartmouth College
Delaware, University of
Drexel University
Duke University
Emory University
Florida International University
Florida State University
Florida, University of
George Mason University
George Washington University
Georgetown University
Georgia State University
Georgia Tech Research Corp
Georgia, University of
Harvard University
Hawaii, University of
Houston, University of
Illinois, University of
Indiana State University
Indiana University
Iowa State University
Iowa, University of
Johns Hopkins University
Kansas State University
Kansas, University of
Kent State University
Kentucky, University of
Lehigh University
Life Sciences Research Foundation
Louisiana State University
Marine Biological Laboratory
Maryland, University of
Massachusetts Institute of Technology
Massachusetts, University of
Miami University
Miami, University of
Michigan State University
Michigan Technical University
Michigan, University of
Minnesota, University of
Mississippi State University
Missouri University of Science
Missouri, University of
Montana State University
National Academy of Sciences
National Aeronautics and Space Administration
National Institute of Standards and Technology
National Science Foundation

Nebraska, University of
Nevada, University of
New Jersey Institute of Technology
New Jersey-Rutgers, State University of
New Mexico State University
New Mexico, University of
New York University
New York, State University Research Fund, Purchase College
New York-Binghamton, State University of
New York-Buffalo, State University of
New York-City College, City University of
New York-Hunter College, City University of
New York-Lehman College, City University of
New York-Queens College, City University of
New York-Stony Brook, State University of
New York-Syracuse, State University of
North Carolina Central University
North Carolina State University
North Carolina, University of
North Dakota State University
North Texas, University of
Northeastern University
Northern Illinois University
Northwestern University
Notre Dame, University of
Ohio State University
Ohio University
Oklahoma State University
Oklahoma, University of
Oregon State University
Oregon, University of
Pennsylvania State University
Pennsylvania, University of
Pittsburgh, University of
Portland State University
Princeton University
Purdue University
Rensselaer Polytechnic Inst.
Rice University, William Marsh
Richmond, University of
Rochester, University of
Salk Institute for Biological Studies
San Diego State University
Scripps Research Institute
South Carolina, University of
South Florida, University of
Southern California, University of
Southern Illinois University
Stanford University
Stony Brook University
Temple University
Tennessee, University of
Texas A&M University
Texas Tech University
Texas, University of
Texas, University of El Paso
Toronto, University of
Tufts University
Tulane University
U.S. Department of Agriculture
Utah State University
Utah, University of
Vanderbilt University
Vermont, University of
Virginia Commonwealth University
Virginia Polytechnic Inst. And State U.
Virginia, University of
Washington State University
Washington University, St. Louis
Washington, University of
Wayne State University
West Virginia University
Western Michigan University
William and Mary, College of
Wisconsin-Madison, University of
Wisconsin-Milwaukee, University of
Woods Hole Oceanographic Institution
Wright State University
Wyoming, University of
Yale University

DOE National Laboratories

Ames Laboratory
Argonne National Laboratory
Brookhaven National Laboratory
Jefferson Lab
Lawrence Berkeley National Laboratory
Lawrence Livermore National Laboratory
Los Alamos National Laboratory
National Renewable Energy Laboratory
Oak Ridge National Laboratory
Pacific Northwest National Laboratory
Sandia National Laboratories-Albuquerque and Livermore
Savannah River National Laboratory
SLAC National Accelerator Laboratory

I. MATERIALS SCIENCES AND ENGINEERING DIVISION

Biomolecular Materials

Institutions Receiving Grants

Multicomponent Protein Cage Architectures for Photocatalysis

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Students:	0 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding:	$220,000

PROGRAM SCOPE

The primary goal of the project is to develop protein-templated approaches for the synthesis and directed assembly of semiconductor nanomaterials and dyes 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) and coordination polymers 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 organic or inorganic materials, 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 semi-conductor material of interest.

FY 2012 HIGHLIGHTS

We have built on our previous success in nucleating the formation of CdS and ZnS nanocrystals on the exterior of P22 and demonstrated the feasibility of employing scaffolding-fusion proteins to nucleate internal nanocrystal formation. Fusion scaffolding proteins were designed based on the observation that an N-terminally deleted version of the 303 amino acid scaffolding protein spanning residues 141-303 was capable of promoting assembly both *in vivo* and *in vitro*. Using standard molecular biology techniques, coding sequences encoding short peptides reported to bind TiO_2 or CdS were introduced at the N-terminus of the coding sequence of the 141-303 scaffolding protein deletion. Both the TiO_2 and CdS, grown under ambient conditions, are observed to be crystalline. More significantly, preliminary results indicate that the rutile rather than the anatase phase is crystallized for TiO_2, which generally requires high temperatures (> 500°C) to produce using traditional synthesis methods.

Engineering the Interface Between Inorganic Materials and Cells

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Sr. Investigator(s):	
Students:	0 Postdoctoral Fellow(s), 3 Graduate(s), 0 Undergraduate(s)
Funding:	$185,000

PROGRAM SCOPE

Cells perform numerous functions, including energy capture, storage, and transduction and the conversion of chemical to mechanical energy during transport. Any adaption of cells and these fundamental processes to DOE goals (e.g., environmental bioremediation, energy harvesting, energy transduction, and biosensing) will require them to function outside of their native environment, as components of hybrid cell-material systems. Since most interfaces with inorganic materials are inherently unnatural, the goal of this work will be to provide the fundamental underpinnings for such systems by developing novel and broadly applicable approaches to engineer both the materials and the cells in order to achieve effective integration. In particular, the proposed work will focus on engineering the interface between inorganic materials (gold and silica) and three model cell types (neural stem cells, fibroblasts, and neutrophils). We will investigate and optimize a range of cellular behaviors and functions, including adhesion, proliferation, migration, and chemotaxis (the latter two constituting behaviors that fundamentally involve the conversion of chemical energy into mechanical energy). Both sides of the interface will be controlled through a parallel and integrated effort to engineer the material and the cells to analyze and regulate cell function. Our work will provide fundamental insight into the interactions of cells with tethered peptides and proteins. We will also explore a variety of cellular engineering efforts to promote cell adhesion, proliferation, migration, and chemotaxis on “pristine” inorganic materials. The ability to promote cell robustness, viability, and function on inorganic materials will be critical for designing the hybrid cell-materials systems of the future.

FY 2012 HIGHLIGHTS

As discussed in our original proposal, optimizing cell function in hybrid “living materials” would greatly benefit from novel approaches to render cells responsive to novel “orthogonal” cues. Our approach makes use of the photoreactive PHR domain from the cryptochrome 2 (CRY2) protein. It was shown in one report that CRY2 can, under some circumstances, homo-oligomerize in response to light in its host plant organism, *Arabidopsis*. A number of cellular signal transduction events involve protein oligomerization. We anticipated that fusion of CRY2 to several proteins whose oligomerization has implicated in the activation of key signaling pathways may enable light-mediated control over these signaling pathways, and downstream cellular behavior. For example, exposure of cells expressing the CRY2-mCherry fused to the receptor protein LRP6 to blue light induced the oligomerization of the protein and the downstream activation of the canonical Wnt pathway. In addition, we have engineered this system to enable light-control over signaling by Rho GTPases. These results are currently under review for publication. In addition, these capabilities are now being explored to determine whether the technology can serve as a general platform to modulate protein assembly and structure inside cells and activate numerous signaling activities in a light-responsive manner, including pathways that can mediate cell adhesion to inorganic material surfaces.

Dynamic Self-Assembly: Structure, Dynamics,and Function Relations in Lipid Membranes

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Principal Investigator:	Parikh, Atul
Sr. Investigator(s):	Sinha, Sunil, California-San Diego, University of
Students:	1 Postdoctoral Fellow(s), 3 Graduate(s), 2 Undergraduate(s)
Funding:	$327,000

PROGRAM SCOPE

We have two over-arching objectives for the proposed work. First, we seek to abstract a physical science-based understanding of fundamental rules that determine dynamic self-assembly processes in lipid bilayer membranes - a versatile class of biologically inspired interfacial complex fluids. Second, our longer-term objective is to translate these physical principles into quantitative design rules for the development of new classes of materials that exhibit complex, cooperative, and adaptive behavior. Our approach is primarily experimental. We employ assemblies of lipid mixtures (e.g., supported lipid bilayers, vesicles, and lipid multilamellae) exhibiting pre-determined physical-chemical properties (e.g., chemical composition, transition temperatures, and curvatures) and examine their spontaneous mesoscopic organization and dynamic remodeling in response to external perturbations. We study the organization of mixed lipid bilayers in the presence of constraints including spatial compartmentalization and asymmetry (structural and chemical) across the bilayer leaflets. The dynamic remodeling is examined under extraneously imposed physical-chemical conditions including (1) interfacial hydration gradients, (2) imposed curvatures, and (3) lipid-specific chemistries. These dynamic structural reorganizations are characterized using spatially- and temporally-resolved microscopy and spectroscopy (wide-area and total internal reflection based fluorescence, ellipsometric, vibrational) techniques. Sunil Sinha at UC San Diego collaborates with us in all experiments and contributes structure characterization using a combination of x-ray reflectivity, x-ray photon correlation spectroscopy, and neutron reflectivity measurements.

FY 2012 HIGHLIGHTS

Substantial progress, detailed in many archival publications, was made during the Fiscal Year 2012 toward each of the objectives, one of which is highlighted below. We have found that in membrane multilayers, prepared from laterally phase-separating lipid mixtures, a remarkable columnar order emerges from the coupling of two-dimensional intralayer phase separation and interlayer smectic ordering. This coupling propagates across hundreds of membrane lamellae, producing long-range alignment of phase-separated domains. Quantitative analysis of real-time dynamical experiments reveals that there is an interplay between intralayer domain growth and interlayer coupling, suggesting the existence of cooperative multilayer epitaxy. We postulate that such long-range epitaxy is solvent-assisted, and that it originates from the surface tension associated with differences in the network of hydrogen-bonded water molecules at the hydrated interfaces between the domains and the surrounding phase. Our findings might inspire the development of self-assembly-based strategies for the long-range alignment of functional lipid domains. This work is accepted for publication in Nature Materials, Dec. 2012 issue and will be highlighted by a cartoon on the Front Cover of the issue.

Bioinspired Hydrogen Bonding-Mediated Assembly of Nano-Objects toward Adaptive and Dynamic Materials

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Sr. Investigator(s):	
Students:	0 Postdoctoral Fellow(s), 2 Graduate(s), 1 Undergraduate(s)
Funding:	$154,000

PROGRAM SCOPE

Nature has evolved many complex, multicomponent materials having adaptive and responsive properties for energy efficiency purposes. For manmade materials, it is highly desirable to harness such dynamic properties for energy efficient applications. Inspired by Nature, this proposal details our plan of developing H-bonding-mediated self-assembly of nano-materials having adaptive and dynamic properties for energy relevant applications. The approach we propose here is to use strong, reversible H-bonding mediators to achieve dynamic nano assemblies. A series of quadruple H-bonding mediators, both for self-complementary and orthogonal, will be synthesized, which are subsequently attached to various nano-objects including carbon-based (C60 & CNTs), metallic (GNPs), and inorganic nanoparticles (SNPs). The functionalized NPs will be dynamically assembled both into 1-D polymer chains and 3-D networks. H-bonding mediated dynamic assembly of those functionalized nano-objects will be carefully investigated in solution, film, and macroscopic solid state. We will systematically tune a number of structural and experimental parameters, including the type and size of nano-objects, the category and density of H-bonding mediators, the length and flexibility of the linker connecting the H-bonding units to the nano cores, and the processing condition for inducing the nano assembly (e.g., solvent, temperature, and time). The adaptive and dynamic properties, including self-healing capability, will be systematically investigated. Building upon successes from this proposed study, in future studies a similar concept can be applied to various other nano systems for the dynamic assembly of complex, multicomponent nano systems having truly multi-functional and environmentally adaptive, self-healing materials.

FY 2012 HIGHLIGHTS

In this year, we have achieved two major breakthroughs in designing dynamic/self-healing polymeric materials. (1) We succeeded in a new design of strong polymeric material able to spontaneously repair itself, without any external help from light, heat, healing agents, or plastizers/solvents. The key to the success is the hard/soft multiphase nanophase morphology which combines the advanced mechanical properties of nanocomposites with the dynamic self-healing features of supramolecular assembly. This work was published in *Nature Chemistry* and highlighted by *Chemical & Engineering News*, http://cen.acs.org/articles/90/i14/Polymer-Heal-Thyself.html. (2) We demonstrated the first example of self-healing polymer using olefin metathesis via dynamic covalent bond exchange. In bulk the material also exhibits unusual malleability due to dynamic C=C double bond exchange. The work was published in the *Journal of American Chemical Society* and highlighted by *Chemical & Engineering News*, http://cen.acs.org/articles/90/i33/Polymer-Healing-Olefin-Metathesis.html.

Bio-Inspired Routes for Synthesizing Efficient Nanoscale Platinum Electrocatalysts

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Sr. Investigator(s):	Wang, Joseph, California-San Diego, University of
Students:	2 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$230,000

PROGRAM SCOPE

The proposed research will focus on the controlled bottom-up biochemical synthesis of highly efficient electrocatalytic platinum nanocrystals through a rational biochemical design. By tuning the biochemical input, we expect to tailor the size, shape, and crystal orientation of the resulting platinum nanocrystals, and hence to maximize their electrochemical reactivity. We will employ specially-designed peptides to promote and control the growth and morphology of platinum nanocrystals through binding to specific crystal planes of platinum. We will also study the use of macromolecular scaffolds as templates to probe novel bio-inorganic interfaces for catalysis, including oxygen reduction reaction. In addition, novel microporous electrode materials and nanoparticle supports will be engineered and studied for enhanced fuel cell performance. Through these studies, we will be able to critically evaluate the electrocatalytic activity of bio-conjugated Pt nanostructures as an effect of crystal size, morphology, peptide and polymer orientation and loading on the nanoparticles and the specific bio-inorganic interface.

FY 2012 HIGHLIGHTS

Major accomplishments during the second year include (1) synthesis of amino acid functionalized polyethylene glycol (PEG) polymers to investigate the role of each amino acid for platinum binding, nanoparticle synthesis, and catalysis; (2) synthesis of defined platinum nanoparticles from the amino acid PEG polymers; and (3) development of novel microporous electrode materials and nanoparticle supports for enhanced fuel performance. In the past year, we completed studies analyzing the use of simple short linear chains of polyethylene glycol to synthesize well-defined sub-10 platinum nanoparticles, including cubes and truncated cubes. We furthermore determined that the platinum nanoparticle growth was controlled through the terminal hydroxyl groups on the PEG (HO-PEG-OH) chains that oxidized to carbonyl groups during or after synthesis. When dimethoxy PEG was used in place of HO-PEG-OH, uncontrolled platinum synthesis occurred to generate bulk platinum precipitates. Because only the OH groups at the termini of the polymers influenced particle synthesis and growth, in working electrolytes such as H_2SO_4 the weak carbonyl-platinum interactions could dissociate easily, allowing for effective catalysis of reactions such as oxygen reduction reaction without any pretreatment. Because spectroscopic and synthesis experiments showed that the ethylene oxide backbone of PEG did little to influence platinum nanoparticle nucleation and growth, these polymers became ideal substrates and scaffolds upon which to attach amino acid R groups in order to investigate specific amino acid-platinum interactions with respect to both synthesis and catalysis; and these studies are currently underway. In addition, several accomplishments involving new and advanced electrode materials and nanoparticle supports for fuel cell applications have been achieved during the second year, including the synthesis three-dimensional hierarchical architectures, consisting of monolithic nanoporous gold or silver films formed on highly ordered 3D microporous carbon supports.

Inorganic Control of Biological Self-Assembly: Engineering Novel Biological Architectures and Redox-Active Protein Assemblies

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Sr. Investigator(s):	
Students:	0 Postdoctoral Fellow(s), 3 Graduate(s), 3 Undergraduate(s)
Funding:	$200,000

PROGRAM SCOPE

The goals of this project are to (1) utilize combined inorganic and protein engineering approaches for the construction of discrete or 1- 2- and 3-D protein superstructures and frameworks, using folded proteins as building blocks and metals as interfacial joints; and (2) exploit the extensive non-covalent interactions formed around the interfacial metal sites within these protein frameworks to control the metal reactivity in ways not accessible in current synthetic inorganic and bioinorganic methodologies. These goals combined will lead to the chemically controllable self-assembly of well-ordered superstructures 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. The significance of the ability to understand and control protein self-assembly cannot be overstated: proteins represent the functionally and structurally most versatile molecular building blocks available to an organism or to a chemist; their self-assembly provides a direct access to the “nanoscale” (2-100 nm) not accessible by top-down approaches and not easily achieved by bottom-up approaches using other types of building blocks; and their assembly into periodic arrays is an absolute necessity for diffraction-based structure determination methods and therefore a driving force for all biosciences. Nevertheless, the mastery over the self-assembly of proteins has not yet reached a level where discrete or infinite architectures with long-range order can be engineered.

Our goals of using metal coordination chemistry to direct protein self-assembly and then to tune the reactivity of interfacial metals are approached at several different levels. These include the design and synthesis of natural and non-natural metal-chelating motifs on protein surfaces to control metal coordination; protein engineering and computational design; structural characterization of superprotein assemblies through crystallography, electron, fluorescence, and atomic force microscopy; and the characterization of metal reactivity and photophysics through an armament of static and time-resolved spectroscopic methods.

FY 2012 HIGHLIGHTS

We have engineered, for the first time, a protein that can self-assemble in a chemically controlled fashion into 1D helical nanotubes, and 2- and 3-D arrays with crystalline order. We have also demonstrated the ability to control the assembly of natural cage-like proteins (like ferritin) through engineered chemical triggers. Next, we plan to chemically control protein self-assembly to better understand protein crystallization processes and to create functional protein-based devices.

Rigid Biopolymer Nanocrystal Systems for Controlling Multicomponent Nanoparticle Assembly and Orientation in Thin Film Solar Cells

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Sr. Investigator(s):	
Students:	1 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$150,000

PROGRAM SCOPE

The project seeks to direct the assembly of nanoparticles into 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 have 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 a seed layer that can nucleate successive layers of single nanocrystals with long-range order and tunable crystallographic orientations. The work will elucidate how particle-DNA interactions influence nanoparticle crystallographic orientation, how nanoparticles on patterned arrays of biomolecules can nucleate long-range order, and how to synthesize 2- and 3-D superlattice arrays of DNA conjugated semiconductor nanocrystals.

FY 2012 HIGHLIGHTS

Prior to the start of this proposed research, the PI has made significant discoveries toward obtaining highly ordered arrays of gold nanoparticle thin films on surfaces. The lessons gained from these studies were an integral part of the proposed DOE research, as they have enabled engineering well-ordered binary semiconductor nanocrystal arrays on surfaces for thin film solar cells. In order to apply the Au NP biomolecular assembly process toward semiconductor materials, however, methods were needed to synthesize DNA-conjugated semiconductor nanoparticles. In the first year, the PI has studied and created different methods to successfully conjugate semiconductor nanoparticles (CdSe, CdTe, CdS) with DNA. Methods were developed to coat the particles with multiple ligands and maintain their stability in the high magnesium concentrations required for DNA assembly. In addition to these studies, thin films of DNA conjugated CdSe quantum dots devices have been fabricated and tested. Initial device designs include fabricating ITO/TiO_2/DNA-CdSe/Au thin film devices. Initial tests show that high photocurrent densities can be produced indicating the DNA is not acting as a strongly insulating material.

Biological and Biomimetic Low-Temperature Routes to Materials for Energy Applications

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Sr. Investigator(s):	
Students:	2 Postdoctoral Fellow(s), 1 Graduate(s), 2 Undergraduate(s)
Funding:	$350,000

PROGRAM SCOPE

The objectives of our research have been three-fold: (1) to conduct further 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; (2) to use our biologically-inspired, low-temperature, kinetically-controlled catalytic synthesis method to optimize the nanostructures and performance of anodes and cathodes for high-performance batteries; and (3) to use our biologically-inspired, low-temperature, kinetically-controlled catalytic synthesis method to further control the structures and properties of the layered cobalt hydroxides, analyzing these structures at the atomic level at DOE synchrotron and neutron diffraction facilities, and analyzing the performance of these materials as a function of structure, seeking to predictively control their local ordering and the distribution of metal-coordination states, and to understand and optimize the structural basis of their magnetic behaviors.

FY 2012 HIGHLIGHTS

(1) In our genetic engineering of silicatein, an enzyme protein that we previously discovered responsible for making the silica skeletons of marine sponges, we accelerated the processes of mutation and natural selection in a test tube to evolve proteins that catalyze the synthesis of semiconductors from aqueous solutions at low temperature. Through this “directed evolution,” we developed new forms of the enzyme capable of producing semiconductors never before produced by living organisms. Starting with DNA encoding the synthesis of silicatein, we introduced mutational changes in the DNA, and then used a high-speed laser to recognize and select those mutants that produced new forms of the enzyme that catalyze the synthesis of novel semiconductors such as titanium dioxide and cadmium selenide. Because these semiconductors are toxic to living cells, the mutagenized DNA strands were introduced into microscopic bubbles of liquid that acted as surrogates of living cells. These microscopic surrogates of cells contained all the constituents of living cells needed to express the mutant DNA molecules, synthesize the new silicatein molecules encoded by the DNA mutants, and—for the few new silicateins with exactly the right structure—support the catalytic synthesis of the new semiconductors.

(2) Based on the mechanism of catalytic synthesis of semiconductors we discovered in silicatein (cf. above), we developed a biologically-inspired, low-temperature, kinetically-controlled catalytic method for the synthesis of a wide variety of nanostructured semiconductors and nanocrystalline metals. We used this method to produce nanocomposite anodes and cathodes for high-performance lithium ion batteries with rate-capabilities (power) higher than components made by conventional processes.

(3) Using this bio-inspired, low-temperature, kinetically-controlled catalytic method, in conjunction with the synchrotron and neutron scattering facilities of DOE national laboratories, we demonstrated kinetic

control of the atomic structures, metal coordination, and spin-coupling states in a family of hydrotalcite-like layered cobalt hydroxides. We showed that kinetic control of this catalytic synthesis and the resulting structures gives unique access to photovoltaic, photocatalytic, magnetic, and photomagnetic behaviors of these materials.

Miniaturized Hybrid Materials Inspired by Nature

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Funding:	$250,000

PROGRAM SCOPE

Our objectives are to develop a fundamental science base for the understanding of lipid- and protein-based assembly in reconstituted biological systems and biomimetic systems with custom-synthesized functional molecules. Our goals are achieved by studying complex collective interactions and their resulting structures in systems mimicking assembly processes occurring in cells on multiple length scales from angstrom to micrometer.

FY 2012 HIGHLIGHTS

Recently we discovered an entirely new class of liposomes, termed block liposomes, resulting from a stimuli-induced membrane shape evolution process. Block liposomes are comprised of distinctly shaped, yet connected, nanoscale spheres, tubes, or rods. The dynamical membrane shape evolution process leading to their formation results from a custom-synthesized, highly charged dendritic lipid (i.e., the stimulus). It remarkably mimics similar membrane shape changes occurring in cells—far from equilibrium—as a result of the action of curvature-generating proteins, which enable specific cell functions such as vesicle budding in endocytosis and intra-organelle trafficking. One of our aims is to elucidate the physical-chemical properties of the novel lipids responsible for block liposome formation. In particular, a series of custom-synthesized lipids will be used to distinguish between the separate contributions of lipid headgroup charge and steric size in stabilizing block liposomes.

Long Range van der Waals-London Dispersion Interactions for Biomolecular and Inorganic Nanoscale Assembly

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Funding:	$167,000

PROGRAM SCOPE

Successful manipulation of nanoscale objects to assemble mesoscale devices is a critical path to innovative energy technologies. A bridge is needed between the nano- and meso-scales where interactions and assembly are controlled, not just through chemical bond formation, but also by the primary long range interactions: van der Waals-London dispersion (vdW-Ld), polar, and electrostatic. The ability to harness the vdW-Ld, electrostatic, and polar interactions is critical in defining the structure and performance of mesoscale structures from nanoscale objects. Due to the lack of measured or calculated optical properties and the lack of an ability to address the realistic geometry of nano- and mesoscale objects, the vdW-Ld interaction has been poorly characterized, rendering nanoscale and mesoscale material design unnecessarily intractable. Now, however, we are learning to direct vdW-Ld forces to guide the design and assembly of new heterogeneous inorganic and biomolecular materials.

In our collaborative project, involving Case Western Reserve University, University of Massachusetts-Amherst, and University of Missouri-Kansas City, we use first principles (*ab initio*) methods, with vacuum ultraviolet spectroscopy, spectroscopic ellipsometry to determine spectral optical properties of materials to construct biomolecular/inorganic systems for new energy technologies encompassing energy efficiency, generation, and storage. The spectral properties of the materials in multiple configurations determine long-range interactions to compare with our measured interaction from light and small angle x-ray scattering experiments. This is particularly pertinent to polar liquids, such as water, with large contributions at low frequencies. The source materials are (bio)polymers, for example, single and double-stranded DNA, proteins such as collagen, and inorganic materials such as silica and aluminum phosphate.

FY 2012 HIGHLIGHTS

In the current period (July 1, 2011 to September 30, 2012), we used previously calculated optical dispersion spectra of 64 different carbon nanotubes and computed the magnitude of vdW-Ld interactions. In an RSC Advances review in press, we provide predictive design tools for manipulating the vdW-Ld interactions of carbon nanotubes. We also hosted a Long Range Interactions Workshop and short course at CWRU in August 2012 to kick off this collaboration and have hosted the seminars for public viewing.

We have initiated spectroscopic ellipsometry studies of bulk DNA films from our UMass collaborators. We are comparing the role of excitons on vdW-Ld interactions in silica glass from experimental and ab initio calculations. The VUV-LPLS reflectance spectroscopy for application to collagen and DNA is advancing, and second virial coefficients determined by multiple angle light scattering will be initiated upon the arrival of the scatterometer.

NA-Mediated Evolution of Catalysts for the Production and Utilization of Alternative Fuels

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Funding:	$250,000

PROGRAM SCOPE

We are developing new methods for the discovery of catalyst materials for use in the production and utilization of alternative fuels. The central premise of the project is that biological macromolecules can evolve in response to selection pressures to synthesize materials with desired catalytic activities. The biological macromolecule used in the project is RNA, and RNA containing key chemical modifications that enhance its catalytic activity. Through a process known as RNA *in vitro* selection, we have shown that RNA sequences can evolve to mediate the formation of new materials. Our primary objective is to apply these methods to the discovery of materials for H_2 production and oxidation and the conversion of CO_2 to hydrocarbon fuels.

FY 2012 HIGHLIGHTS

RNA *in vitro* selections have now been performed in our labs to discover unique sequences that can mediate the growth of Pt, Pd, and iron oxide nanoparticles. In studying individual sequences that emerged from these selections we have observed sequence-dependent control over particle size, shape, and composition. In the past year, we also made the surprising discovery that the crystallinity of nanoparticles formed from solutions containing RNA depends upon the presence of sequence mixtures. That is, a single sequence selected from the original random RNA sequence library produced very poorly crystalline Pd nanoparticles, while a combination of sequences that emerged from the selection yielded crystalline nanoparticles. To our knowledge, this is the first example in which two biomolecules (RNA, DNA, or peptides) selected *in vitro* work together to provide a unique chemical outcome.

Assembling Microorganisms into Energy Converting Materials

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Funding:	$150,000

PROGRAM SCOPE

This project aims to integrate 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 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. The objective is to create robust and scalable energy conversion materials using bacterial spores as the key biomolecular material responsible for energy conversion. We are going to use a suite of experimental platforms, including atomic force microscopy and micro-electromechanical systems, 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.

FY 2012 HIGHLIGHTS

We have started atomic force microscopy-based measurements to investigate maximum actuation pressure and strain levels of spores. We have developed an experimental setup to control relative humidity near the atomic force microscope cantilever in a dynamic manner, and we have identified cantilever probes and tip geometries suitable for measuring the mechanical response of spores. Preliminary work density measurements have been performed. We are now extending our measurements to different species.

DNA-Grafted Building Blocks Designed to Self-Assemble into Desired Nanostructures

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Funding:	$454,412

PROGRAM SCOPE

This program is aimed at developing transformative, hybrid genetic algorithm-based, modeling tools, validated by novel experiments, for designing DNA-grafted colloidal building blocks that will spontaneously and reliably self-assemble into desired crystal structures. Traditionally, the creation of ordered nanostructures involves a trial-and-error approach; colloidal building blocks are first synthesized (or constructed on a computer) and then examined as to the structures they assemble under desired processing conditions. These experimental/modeling strategies encounter two classes of difficulty. First, these Edisonian trial-and-error methods are laborious and expensive, and do not allow us to design nanoparticles that can assemble into a desired structure. Second, the growing avalanche of data from high throughput experiments and computer simulations from the Edisonian approach have created an informatics challenge for material design and discovery.

To make progress in this field, we make a break from current practice and propose a new “inverse” paradigm that increases the idea flow, broadens the search horizon, and archives the knowledge from today’s successes to accelerate those of tomorrow. A primary feature of our approach is that we shall develop hybrid genetic algorithm based methods that will allow us to replace the trial-and-error methodology (forward problem) with one that can design a building block that will spontaneously assemble into a desired structure (inverse problem). While our model predictions, which will be critically validated against novel experiments, will potentially transform this field, the more important point is that this new methodology can eventually revolutionize the whole field of materials design.

To accomplish our ambitious goals, we have assembled a team of expert PIs with complementary experimental and theoretical skills who are crucial to its success. Kumar (forward modeling), Gang (experiments), Venkatasubramanian (GA modeling), and Collins (advanced machine learning algorithms) have recently begun to collaborate on *a-priori* design DNA-grafted nanoparticles that will spontaneously assemble into ordered arrays. The addition of the critical design component will allow this team to begin to focus their studies on systems of particular interest in the context of applications.

Optimizing Immobilized Enzyme Performance in Cell-Free Environments to Produce Liquid Fuels

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Funding:	$120,000

PROGRAM SCOPE

Immobilization of enzymes has gained prominence in the last few decades due to its vast industrial applications, for example, manufacture of bio-fuels. But, immobilization of enzymes results in reduced enzymatic activity. The reduced activity is attributed to the structural rearrangements of the enzyme on the immobilizing surface. The main objective of this project is to get a better understanding of the physics of protein folding and reactivity on different surfaces and degree of confinement. Our studies indicated that proteins having a well defined native structure in bulk were stabilized upon confinement when the confining surface was neutral, whereas they lost their secondary structure when the confining walls were made hydrophobic. We want to extend this study to enzyme catalyzed reactions under confinement and crowding. Reaction ensemble Monte Carlo simulations were employed to study bimolecular association and ligand substrate binding reactions. Effects of pore size and surface interactions are also studied.

FY 2012 HIGHLIGHTS

We studied the stability of proteins inside a hydrophobic cavity at different degrees of confinement and surface hydrophobicity. We observed that proteins having a well defined secondary structure lost their secondary structure upon adsorption onto a hydrophobic surface, whereas intrinsically disordered proteins gained structural and thermal stability upon adsorption on a hydrophobic surface. This result was published in the *Journal of Chemical Physics* [M. Radhakrishna, S. Sharma, and S. K. Kumar, J. Chem. Phys. 136, 114114(2012)].

RECOVERY ACT - Directed Assembly of Hybrid Nanostructures Using Optically Resonant Nanotweezers

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

PROGRAM SCOPE

In this research, we are performing a theoretical and experimental investigation into the assembly of hybrid nanomaterials and nanostructures using nanophotonically directed optical forces. 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 and proteins) and non-biological (nanoparticles) materials as small as a few nanometers in size. Here we will be to extend this technique to enable the directed assembly of hybrid nanostructures that cannot be manufactured by other means (e.g., self-assembly or chemical synthesis). Although we focus our work here on understanding some of the fundamental physics behind this new approach, we envision the ultimate implementation of the technique could be a form of “optical nanofactory” that could assemble arbitrary materials from constituent parts. An example of what we hope to do here is use an optically resonant nanotweezer to thread gold nanoparticles inside a single carbon nanotube. We envision that structures created with this technique could yield unique high efficiency photo-electric or photo-thermal energy conversion devices and enable more precise studies of the fundamental structure of nanomaterials.

FY 2012 HIGHLIGHTS

We have demonstrated the ability to trap and rotate carbon nanotubes and microtubules. This was the first demonstration of our ability to actively rotate an elongated particle, which is a key requirement for enabling the assembly described above. The paper describing these results, accepted for publication in the journal *Nano Letters*, contains details of the experimental results as well as a theoretical interpretation.

(Bio)Chemical Tailoring of Biogenic 3-D Nanopatterned Templates With Energy-Relevant Functionalities

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Funding:	$299,999

PROGRAM SCOPE

The overall aim of this research has been to obtain fundamental understanding of (bio)chemical methodologies that will enable utilization of the unique 3-D nanopatterned architectures naturally produced by diatoms for the syntheses of advanced catalytic and structural materials attractive for applications in bio-energy conversion and energy storage. The research is being conducted in three research thrusts. Thrust 1, mechanistic analysis of *in vivo* immobilization of proteins in diatom biosilica, is directed towards elucidating the fundamental mechanism(s) underlying the cellular process of *in vivo* immobilization of proteins in diatom silica. Thrust 2, mechanistic analysis of shape-preserving reactive conversion of diatom biosilica into high-surface area silicon replicas, is aimed at understanding the fundamental mechanism of shape preservation and nanostructure evolution associated with the reactive conversion of diatom biosilica templates into high surface area inorganic replicas. Thrust 3, immobilization of energy-relevant enzymes in diatom biosilica and onto diatom biosilica-derived inorganic replicas, involves use of the results from both Thrust 1 and 2 to develop strategies for *in vivo* and *in vitro* immobilization of enzymes in diatom biosilica and diatom biosilica-derived inorganic replicas, respectively.

FY 2012 HIGHLIGHTS

Progress has been made in all three research thrusts associated with this overall aim. In Thrust 1, further insight into the structure of the targeting peptide required for *in vivo* incorporation in diatom silica has been obtained. The penta-lys-cluster of tpSil1 has been found to act as a highly efficient silica targeting signal (STS). An artificial penta-lys-cluster, consisting only of lysine and serine residues within a 14 amino acid sequence, also exhibited STS activity; and the reporter protein (GFP) was found to be present throughout the girdle band region. These results demonstrate that lysine and serine residues are crucial components of the STS. In Thrust 2, additional fundamental understanding of (1) the shape-preserving gas/solid magnesiothermic reaction of silica (for use in generating highly porous silicon diatom replicas for battery applications) and (2) the conversion of diatom silica into high surface area C and C/Pt replicas (for use as an electrode for the oxygen reduction reaction in polymer electrolyte fuel cells) and metallic (Au, Cu) replicas has been obtained. XRD, SEM, and TEM analyses have provided insights into the kinetic mechanism of reaction, the mechanism of stress relaxation, and the nanostructural evolution associated with the relevant gas/solid reactions. In Thrust 3, the scope of the LiDSI method has been investigated for enzymes that require oligomerization, cofactors, and posttranslational modifications for activity. Furthermore, chemical and physical parameters that determine the *in vitro* incorporation of the energy-relevant enzyme glucose oxidase into high surface area replicas of diatom silica have been identified.

Actuation of Bioinspired, Adaptive High-Aspect-Ratio Nano- and Micro-Structures Powered by Responsive Hydrogels: Synthesis and Modeling

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Funding:	$410,000

PROGRAM SCOPE

From the simplest bacteria to mammals, survival is dependent on the organism’s ability to extract meaningful information from a noisy environment. To accomplish this critical task, various animals have developed sensory systems based on arrays of hair-like structures that act as mechanoreceptors. These exceptional mechanosensory systems motivate and inspire our studies. The ability to “engineer” adaptiveness into the next-generation devices is becoming a key requirement and challenge in materials science. The goal of this project is to develop versatile synthetic and fabrication methods compatible with a wide range of materials across different length scales, leading to materials that are multifunctional, with finely-tuned geometry, chemistry, and mechanics, and capable of actuation in response to a variety of stimuli, including temperature, humidity, and magnetic, electrical, mechanical, and chemical cues. The creation of this novel class of actuatable nano- and micro-structured materials will enable the bio-inspired design of new components and functions, especially involving motion, propulsion, responsiveness, self-assembly, and dynamic control at the nano/micrometer scale. Our experimental work is integrated with computational studies that help explain the experimental results and guide new developments.

FY 2012 HIGHLIGHTS

We have developed a robust electrodeposition method for changing the shape and aspect ratio of microstructures, allowing us to create a multitude of masters for further replication—without resorting to expensive and laborious lithographic top-down methods. We have been exploring and exploiting a multiphoton lithography (MPL) approach to generating hybrid actuation systems to pattern pH- and temperature-responsive hydrogels. MPL also allows us to pattern catalytic Pt and Pd microstructures and integrate such catalysts within three-dimensional microenvironments, which is essential for the design of more intricate dynamic systems. We have designed a new materials platform that can mediate a variety of chemo-mechano-chemical processes, with a possibility to build-in homeostatic feedback loops. The system reversibly transduces external or internal chemical inputs into user-defined chemical outputs via the "on/off" mechanical actuation of microstructures. The complex behavior of filamentous hydrogel-muscle-embedded structures in response to stimuli has been extensively computationally modeled, providing us with better understanding and predictive abilities. The work was published in top scientific journals, such as *Nature*, *Soft Matter, JACS, Nature Protocols, Nano Letters, Small*, *Nano Today*.

Dynamic Self-Assembly, Emergence, and Complexity

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Funding:	$300,000

PROGRAM SCOPE

The focus of this research program is the study of complex systems. We define a complex system—following the definition common in physics—as one comprising components interacting dissipatively. *Components* and *interactions* can be virtually anything; the *dissipative* constraint ensures that the system is out of equilibrium and almost certainly shows, for some number of components, the influences of nonlinear effects. Complex systems, as they evolve, commonly show unexpected (often called *emergent*) behaviors. Understanding these behaviors illuminates the nature of such dissipative, out-of-equilibrium systems, and also serves as a superb tool for a discovery.

The program has four general goals:

(1) To build (e.g., in chemical terms, to synthesize) complex systems, by selecting and characterizing individual components, adding them to the system one at a time, and observing the appearance of unexpected behaviors and phenomena.

(2) To rationalize—in so far as possible—these behaviors/phenomena, and to build quantitative or semi-quantitative analytical models for them that reveal the underlying nonlinearities and the physical processes that give rise to them.

(3) To develop a mechanistic understanding (which will often combine analytical, physics-based approaches with more physical-organic, chemically based approaches) of the systems to the point where it is possible to use it to design and build new systems, and to control them rationally, by design.

(4) To identify areas and problems where these systems might be applied, and to prototype (but not fully develop) these applications.

FY 2012 HIGHLIGHTS

Our major efforts have focused on molecular-like phenomena in assemblies of millimeter-sized beads; bubbles and drops; charge transport through self-assembled monolayers; dynamic microfluidic displays for soft machines; actuation of complex motions in soft machines; multiplexed bioassays based on magnetic levitation; and interacting flamelets.

Observation and Simulations of Transport of Molecules and Ions Across Model Membranes

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

PROGRAM SCOPE

Transport of chemical species across membranes has universal importance, for separations, sensors, pharmacological applications, and life itself. We propose to study transport across model membranes by a closely coupled combination of experiments and theoretical simulations, using parallel development of the experimental system and the computer simulations. For the initial studies described here, we will employ lipid bilayers supported on a solid substrate in a unique experimental setup, but the design is sufficiently general that the transport of molecules across other thin film membranes can be investigated. We will study the transport process itself, using our ability to detect chemical species along the transport path: in the bulk medium on one side of the membrane, in the membrane, and in the receiving nanochannel pores on the other side. Concentration profiles of the transportable species in these regions can be obtained in the experimental set-up, and these can be simulated using molecular dynamics techniques, coarse-grained MD in particular. The nature of the experiments and simulations are such that very detailed questions can be asked and answered, permitting fundamental physicochemical characterization of the transport events. The molecular-level details that can be provided by theory are believable only if experiments provide verification in sufficient detail so that theory is held accountable or is bounded by constraints imposed by experimental results. MD simulations can provide details far beyond the experimental observations that transport has occurred and the number of events over a period of time. Typically this would be, for an ion channel, the total charge transported per unit time. In contrast, we can offer much more than this.

FY 2012 HIGHLIGHTS

We have carried out simulations that show how nanoparticles interact with biological membranes. This is of significant importance in determining the toxicity of nanoparticles as well as their potential applications in phototherapy, imaging, and gene/drug delivery. It has been shown that such interactions are often determined by nanoparticle physicochemical factors such as size, shape, hydrophobicity, and surface charge density. Surface modification of the nanoparticle offers the possibility of creating site-specific carriers for both drug delivery and diagnostic purposes.

Nanoparticles are generally considered excellent candidates for targeted drug delivery. However, ion leakage and cytotoxicity induced by nanoparticle permeation is a potential problem in such drug delivery schemes because of the toxic effect of many ions. We have carried out a series of coarse-grained molecular dynamics simulations to investigate the water penetration, ion transport, and lipid molecule flip-flop in a protein-free phospholipid bilayer membrane during nanoparticle permeation. The effect of ion concentration gradient, pressure differential across the membrane, nanoparticle size, and permeation velocity have been examined in this work. Our studies show that significant cytotoxicity can result during a nanoparticle penetration event, in addition to significant cell damage, as a result of lipid flip-flop.

Phospholipid Vesicles in Materials Science

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Funding:	$229,000

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 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 2012 HIGHLIGHTS

Using single-molecule fluorescence imaging, we studied entanglement, the many-chain phenomenon that causes linear macromolecules to diffuse preferentially parallel to their chain contour. Extending this to driven transport, we described a straightforward, automated line tracking method to visualize linear macromolecules as they rearrange shape by Brownian diffusion and under external fields such as electrophoresis. These technical advances enabled broad conceptual progress in understanding the limitations of prevalent views about Brownian diffusion. It is commonly presumed that the random displacements that particles and molecules undergo as a result of the thermal jiggling of the environment follow a normal (or Gaussian) distribution, but we found repeated instances in which the classical expectations failed. Reasoning from study of liposome diffusion in nematic actin solutions, non-Gaussian behavior appeared to span broad time scales; and we were able to propose why exponential step length distributions are frequently observed.

Self-Assembly of PI-Conjugated Peptides In Aqueous Environments Leading To Energy-Transporting Bioelectrical Nanostructures

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Funding:	$210,000

PROGRAM SCOPE

How can we rationally manipulate organic electronic materials in order to realize new technologies? Our group recently developed pi-conjugated peptides that undergo supramolecular self-assembly into one-dimensional organic electronic nanomaterials under benign aqueous conditions. Our objectives for future research are to construct and study new and functional electronic materials for energy-related technology where peptide-driven self-assembly enhances pi-stacking within nanostructured soft materials at size regimes currently out of reach synthetically or lithographically. The pi-stacking leads to defined perturbations of the optoelectronic properties and yields nanoscale conduits that should direct charge migration/separation throughout bulk macroscopic scaffolds. These conduits will be tailored for molecular recognition on the periphery of the supramolecular objects in two very different approaches: (1) by the presentation of residues to sequester metal ions prior to the mineralization or metallization of inorganic materials and (2) by the presentation of oligopeptides that induce cell adhesion. These approaches will help to make connections between nanoscale electronic materials and macroscopic bulk interfaces, be they those of a cell or of a device. Implications for extracting energy from incident solar radiation and for manipulating energy at the biotic-abiotic interface will be addressed.

FY 2012 HIGHLIGHTS

Research over the past fiscal year has been centered on two major fronts. First, validation of a powerful new synthetic approach to prepare pi-conjugated peptides. Rather than synthesize reactive pi-conjugated building blocks up front to use for peptide couplings, we can now synthesize them directly on the peptide synthesis supports. This eliminates difficult syntheses and problematic solubilities encountered or expected for longer oligomeric structures. Using this new approach, we have achieved some of the longest pi-electron oligomers embedded within peptides and explored their aqueous assembly and electronic properties. Second, studies in what we call "supramolecular polymorphism." Using the ease of peptide synthesis to achieve a library of controlled sequence variations, we have explored how the steric bulk and solvation properties of constituent amino acid residues at varied locations relative to the electronic core can influence the observed optoelectronic properties. Although we have yet to extract a predictive model, subtle sequence variations can dramatically influence the intermolecular electronic coupling within a nanostructured material.

Bio-Inspired Architectures for Controlled Adhesion, Friction, and Surface Compliance

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PROGRAM SCOPE

Our aims are to fabricate, study, and model bio-inspired architectures for controlled surface mechanical properties, such as adhesion, friction, and surface compliance. We are particularly interested in how bio-inspired synthetic architectures can be designed with unique properties of natural systems, such as actively controlled adhesion & friction, and selectivity. Our work combines bioinspired design and fabrication of surface architectures, measurement of their properties, and the development of detailed quantitative models.

FY 2012 HIGHLIGHTS

(1) We showed how a 1D array of pillar-channels can be used to endow an elastomeric surface with highly selective recognition and adhesion. We showed that, under optimal conditions, shape-complementary surfaces can have adhesion enhanced by up to a factor of 40 compared to a flat control whereas non-complementary combinations have nearly negligible adhesion. Orientational mismatches were found to be accommodated by interfacial dislocations that also played a significant role in modulating interfacial strength.

(2) We discovered that solid surface tension plays a very significant and hitherto neglected role in determining the shape and deformation of surfaces in compliant solids such as elastomers and hydrogels. Specifically, we studied how surface tension limits what shapes can be formed on the surface of a compliant solid.

(3) We published an extensive review of the field of biomimetic and bioinspired structured interfaces.

(4) We developed a new computational method to handle the mechanics of contact, and extended an experimental method to measure adhesion, between structured surfaces.

(5) We developed surfaces patterned with stripes of charge using polyelectrolyte layers for selectivity through electrostatic complementarity.

High Efficiency Biomimetic Organic Solar Cells

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Funding: $275,000

PROGRAM SCOPE

Organic solar cells are a promising, low cost, solar cell technology. But unlike conventional solar cell materials, organic semiconductors generate localized excitons when they absorb light. The binding energy of these excitons is so large that they cannot be split into charge by the electric field inside a solar cell. Consequently, organic materials require a fundamentally different architecture.

Photosynthesis is the best model for organic solar cells since it shares much of the same physics. In photosynthetic reaction centers, exciton dissociation is achieved through a multi-step electron transfer rather than a single donor-acceptor junction. In this project we address two key questions. (1) *How is charge generated in organic solar cells?* (2) *Will a biomimetic architecture inspired by photosynthesis help efficiency?*

FY 2012 HIGHLIGHTS

We have shown that many organic solar cells have a fortuitous multi-step charge dissociation process arising from polarization changes at the donor-acceptor interface. This helps explain the mystery of why some materials combinations work much better than others and takes us one step closer to rational design of these promising devices.

Self-Assembly and Self-Repair of Novel Photovoltaic Complexes – Synthetic Analogs of Natural Processes

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Funding: $218,000

PROGRAM SCOPE

Chloroplasts solar energy harnessing is the ultimate source of chemical energy in food supplies, oil and plant-derived fuels on the planet. With a maximum glucose production efficiency of 6 %, chloroplasts could provide an abundant and inexpensive alternative to solar cells. However, harnessing this photosynthetic power for solar energy conversion to liquid fuels remains a challenge. The primary goal of the program is to interface chloroplasts' self-repairing photosynthetic processes with synthetic nanomaterials to create bio-inspired constructs with enhanced photosynthesis. We have interfaced plant-derived components with nanostructured complexes to synthesize the first photoelectrochemical complex capable of mimicking key aspects of the plant self-repair cycle. In this setup, a solution consisting of photosynthetic reaction centers, phospholipids, scaffold proteins, single-walled carbon nanotubes, and surfactant spontaneously self-assemble into a photoactive complex, wherein the reaction centers are each embedded into a lipid bilayer. Like plant-based self-assembly, the process is completely reversible. In an alternative study, we synthesized light-harvesting antennas reminiscent of those surrounding the PSII to enhance photo-conversion. The core-shell constructs consisted of large band-gap nanotubes in an outer shell and small, band-gap nanotubes within the fiber core. We recently have taken advantage of chloroplasts' densely-packed arrays of photosystems and antenna complexes to create a biofuel cell with self-repair properties. Despite their ideal photosynthetic structural arrays for solar energy harvesting, chloroplast energy-based devices remain unexplored due to their limited lifetime. We are currently working on the assembly of catalytic nanoparticles with chloroplast self-repairing mechanisms to allow traditionally static solar energy devices to become more economically viable solutions to the energy problem.

FY 2012 HIGHLIGHTS

The incorporation of chloroplasts into synthetic, light-harvesting devices requires regenerative reactive oxygen species (ROS) scavenging mechanisms to prolong photoactivity. We quantitatively examine the effect of dNC, previously demonstrated as a potent ROS scavenger, along with cerium ions, fullerenol, and DNA-wrapped single-walled carbon nanotubes, on isolated chloroplasts ROS generation. We find dNC were unable to penetrate the chloroplast outer envelope but were the most effective of these agents for decreasing oxidizing species and superoxide concentrations whilst preserving chloroplast photoactivity, offering a promising mechanism for maintaining regenerative chloroplast photoactivity for light-harvesting applications. Finally, we demonstrated that the addition of ROS scavengers to chloroplasts preserves their ability for electrochemical energy generation from direct illumination.

Self-Assembling Biological Springs: Force Transducers on the Micron and Nanoscale

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PROGRAM SCOPE

We have discovered that helical ribbons with a fixed pitch angle self-assemble in a variety of quaternary solutions containing the sterol, a mixture of surfactants and water. Our x-ray studies have shown that the cholesterol helical ribbons are single crystal strips wrapped into a helical form. The overall goal of this project is to utilize these novel biomolecular objects as mesoscopic springs and deformation gauges.

We are developing new methods to use these helical ribbons for measuring and applying forces in the pico- and nano-newton range. These are forces characteristic of macromolecular interactions in biological systems. Cholesterol helical ribbons can serve as very soft mesoscopic springs. Depending on their dimensions, they have spring constants ranging from 0.5 to 500 pN/m. The spring constants of all cholesterol helical ribbons can be calculated from their observable geometrical features: width w, contour length s, and radius R. A helical ribbon with a spring constant appropriate for a particular application can be readily selected from a polydisperse ensemble of ribbons formed in solution. To be used for force measurements and force transduction, the ribbon must be attached to the objects under investigation. Direct tethering of cholesterol ribbons is difficult because of its delicacy and absence of chemically active groups on its surface. Various means to modify the surface of the helical ribbons have been explored, and we have found that polydopamine surface coating provides the desired adhesion. In addition, this coating renders the helical ribbons more robust, and also enables further surface modifications such as metal plating. Our helical ribbons are soft and have the same pitch angle in their unstrained form independent of external solution conditions, but can change in response to a local strain. These properties suggest the use of helical ribbons as strain detectors and indicators to measure plastic and elastic deformation in hydro gels.

FY 2012 HIGHLIGHTS

Up to now, we have demonstrated that cholesterol helical ribbon with desirable geometry parameters (i.e., *w*, *s*, and *R*) can be selected using light microscope, and one end of the selected helical ribbon can be readily tethered to the glass capillary which is controlled by a micromanipulator. Our recent results show significant progresses in functionalization of the helical ribbon with biotinylated lipids. Successful biotinylation of helical ribbons allows not only the measurement of the binding force between biotin and streptavidin molecules but also further functionilzation of the helical ribbons. In the next period, we shall implement the first biological force measurement using the cholesterol helical ribbons.

Experimental Realization of 'Repair-and-Go' using Microencapsulation of Nanomaterials

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PROGRAM SCOPE

The purpose of this project is to experimentally validate and implement the concept of localized delivery by a process termed *repair-and-go*, which to this point has been a theoretical challenge that is only now being approached experimentally. We will probe damaged (cracked) structures with nanoparticle-containing microcapsules and identify imperfections in the structures by depositing fluorescent nanoparticles into the cracks, such that evidence of nanoparticle localization is visualized easily by fluorescence microscopy. Moreover, we seek to repair the damaged structures using this technique by coupling polymerization/cross-linking chemistry with material deposition into the cracks. As such, following our initial approach of nanoparticle deposition, we seek to expand the repair-and-go concept to include encapsulation and selective delivery of larger (sub-micron) particles, reactive material such as epoxy adhesives, and a combination of the two towards realizing mechanical repair of damaged substrates. The proposed research will lead to (1) novel polymer surfactant materials for encapsulation, where these polymers cover the surface of droplets and control the release of the droplet contents onto the surface of damaged materials; (2) novel adhesive materials for delivery and substrate repair; and (3) understanding of the extent to which repair-and-go leads to measurable mechanical recovery of damaged materials.

FY 2012 HIGHLIGHTS

The project, starting on September 1, 2012, was initiated by building platform knowledge of the amphiphilic polymers that can be used effectively in the oil-in-water emulsion encapsulation of nanoparticles, and the types of nanoparticles that can be used effectively in this process. In addition to phosphorylcholine-based polymers, sulfobetaine-containing polymers are seen to be useful and offer an additional tool for producing capsules that are responsive to the ionic strength of the surrounding medium.

Long-Range van der Waals-London Dispersion Interactions for Biomolecular and Inorganic Nanoscale Assembly

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Funding:	$330,000

PROGRAM SCOPE

Successful manipulation of nanoscale objects to assemble mesoscale devices is a critical path to innovative energy technologies. A bridge is needed between the nano- and meso-scales where interactions and assembly are controlled, not just through chemical bond formation, but also by the primary long range interactions: van der Waals-London dispersion (vdW-Ld), polar, and electrostatic. The ability to harness the vdW-Ld, electrostatic, and polar interactions is critical in defining the structure and performance of mesoscale structures from nanoscale objects. Due to the lack of measured or calculated optical properties and the lack of an ability to address the realistic geometry of nano- and mesoscale objects, the vdW-Ld interaction has been poorly characterized, rendering nanoscale and mesoscale material design unnecessarily intractable. Now, however, we are learning to direct vdW-Ld forces to guide the design and assembly of new heterogeneous inorganic and biomolecular materials.

In our collaborative project, involving Case Western Reserve University, University of Massachusetts-Amherst, and University of Missouri-Kansas City, we use first principles (ab initio) methods, with vacuum ultraviolet spectroscopy, spectroscopic ellipsometry to determine spectral optical properties of materials to construct biomolecular/inorganic systems for new energy technologies encompassing energy efficiency, generation, and storage. The spectral properties of the materials in multiple configurations determine long-range interactions to compare with our measured interaction from light and small angle x-ray scattering experiments. This is particularly pertinent to polar liquids, such as water, with large contributions at low frequencies. The source materials are (bio)polymers, for example, single and double-stranded DNA, proteins such as collagen, and inorganic materials such as silica and aluminum phosphate.

FY 2012 HIGHLIGHTS

In the current period (July 1, 2011 to September 30, 2012), we used previously calculated optical dispersion spectra of 64 different carbon nanotubes and computed the magnitude of vdW-Ld interactions. In an RSC Advances review in press, we provide predictive design tools for manipulating the vdW-Ld interactions of carbon nanotubes. We also hosted a Long Range Interactions Workshop and short course at CWRU in August 2012 to kick off this collaboration and have hosted the seminars for public viewing.

Ab initio calculations of duplex DNA with varying composition and stacking sequence are in progress. Method developments for large protein calculations are being pursued. Excitonic effects will be studied by comparing ab initio and experimental spectra in silica. Variations in vdW-Ld interactions from spectral truncation and gaps and oscillator modeling will be quantified. Preparation of wet spun DNA films for optical spectroscopy has been accomplished. Force measurements on these samples with different counterions and temperatures reveal entropy as well as force changes with separation.

Simulations of Self-Assembly of Tethered Nanoparticle Shape Amphiphiles

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PROGRAM SCOPE

Self-assembly of nanoparticle building blocks, including nanospheres, nanorods, nanocubes, nanoplates, nanoprisms, etc., may provide a promising means for building functional and useful materials. Extending and employing computer simulation to elucidate the principles of self-assembly and develop a predictive theoretical framework is the central goal of this project.

FY 2012 HIGHLIGHTS

To model increasingly complex shapes with high computational performance, we have pursued the problem of optimal filling of shapes using spheres to *fill* the shape with *N* polydisperse, overlapping *n*-balls without exceeding the boundaries of the shape. Formally, we define the *filling* problem as a question of how to place *N* polydisperse *n*-balls, each contained entirely inside a shape *G* so as to maximally cover the area of *G.* The filling problem is a global optimization problem with a complex solution space. Analytical solutions for arbitrary *N*, such as those desired for use in our simulations, are not tractable. Instead, we turned to numerical nonlinear optimization techniques and developed computer codes that find an approximate optimal filling given any simple polyhedron and any *N*. For a given shape, one needs only to consider solutions where the circles or spheres lie on the shape's medial axis. Extensive classification of the behavior of the solutions led us to several conjectures about the behavior of the solution space. These conjectures enabled smart heuristics to be programmed into the codes that decrease the time spent searching for optimal solutions while at the same time increasing their accuracy and precision. In addition to nanoparticle self-assembly, this work has potential for applications in computer animation, treatment of cancer, advancement of microelectronics, and securing of wireless networks, among others. [Phillips, Anderson, Huber, Glotzer, "Optimal Filling of Shapes," Phys. Rev. Lett., 108 (19), May 2012. DOI: 10.1103/PhysRevLett.108.198304. Press coverage includes APS Spotlighting Exceptional Research 5/10/2012, ScienceDaily.com 5/10/2012, and AoNano.com.]

We extended the basic Molecular dynamics methods in HOOMD-Blue *with rigid body constraints* to enable composite particles with complex shapes such as anisotropic nanoparticles, grains, molecules, and rigid proteins to be modeled. HOOMD-Blue can now simulate systems of particles, rigid bodies, or mixed systems in microcanonical (NVE), canonical (NVT), and isothermal-isobaric (NPT) ensembles. In typical cases, HOOMD-blue on a single GTX 480 executes 2.5-3.6 times faster than LAMMPS executing the same simulation on any number of CPU cores in parallel. Simulations with rigid bodies may now be run with larger systems and for longer time scales on a single workstation than was previously even possible on large clusters. [Nguyen, Phillips, Anderson, Glotzer, "Rigid body constraints realized in massively-parallel molecular dynamics on graphics processing units," Computer Physics Communications, 182 (11), pp 2307-2313, November 2011. DOI: 10.1016/j.cpc.2011.06.005.]

Multicomponent Protein Cage Architectures for Photocatalysis

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Funding:	$253,000

PROGRAM SCOPE

Virus capsids can be used as templates for precise control over the size, spacing, and assembly of molecular and nanomaterial species, resulting in uniform and reproducible nano-architectures. This multidisciplinary effort is aimed towards the development of biomimetic materials, utilizing the bacteriophage P22, for coupled light harvesting and catalysis and an understanding of the underlying photophysical processes.

FY 2012 HIGHLIGHTS

Using the P22 capsid, we have demonstrated the co-encapsulation of green fluorescent protein and mCherry on the interior. This was achieved by genetically fusing the GFP-mCherry and scaffold protein together and co-expressing this poly-protein with coat protein. The Scffold protein templates the assembly of the capsid and directs the encapsulation of this fused cargo. The fusion is packed at very high local concentration (~ 4 mM). Excitation of GFP (at 420 nm) results in energy transfer between these co-encapsulated proteins and results in fluorescence from the mCherry at 610 nm. This work was recently accepted for publication in Biomacromolecules *(*http://dx.doi.org/10.1021/bm301347x). This demonstration of directed co-encapsulation and crowding of energy-matched partners can now be extended to include co-encapsulation and crowding of light harvesting and catalytic partners for energy utilization applications.

A metal-based light harvesting antenna consisting of three ruthenium complexes linked to an electron-deficient cobalt center was prepared as a demonstration of a flexible approach to synthesizing photoactive coordination polymers using click chemistry. This tetranuclear ruthenium(II)-cobalt(III) complex was investigated by steady-state and time-resolved spectroscopy in order to study the feasibility of transferring redox equivalents from the ruthenium complexes to the catalytically active cobalt center. Femtosecond transient absorption measurements combined with time-correlated single-photon counting measurements of emission lifetimes revealed that electron transfer from ruthenium to cobalt takes place in approximately 100 ns. This is consistent with relatively weak superexchange coupling of the triazole-linked phenanthroline ligands that bridge the two metals.

Separate femtosecond transient absorption experiments probed interligand charge transfer in a series of mononuclear ruthenium complexes containing variable numbers of bipyridine and phenanthroline ligands. Linking ruthenium complexes to active metal centers requires the modification of at least one ligand, which can change the properties of the excited states used to initiate energy or electron transfer. The complexes studied differ in their sub-nanosecond excited state dynamics, showing that phenanthroline ligands not only change the MLCT energetics, but also affect the dynamics of excited states associated with the bipyridine ligands. Better understanding of how modified ligands alter the properties of transition metal photosensitizers can be used to improve schemes for funneling energy or charge towards an active site, an essential initial step in photocatalysis.

Electronic Interfacing between a Living Cell and a Nanodevice: a Bio-Nano Hybrid System

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PROGRAM SCOPE

Coupling physical electronics with live cells or microorganisms opens the possibility of leveraging the highly sophisticated functions of a biological system, such as memory, adaptability, and multitasking, to create novel logic circuits, sensors, and new sources of energy. The goal of this (fundamental) research is to take the first steps toward developing these “bio-nano hybrid” systems where the biochemical activity in the cell modulates the electrical response of the physical system, for example, alter its conductivity, i.e., gating. Typically, in a cell, the energy required to fuel endergonic biochemical reactions by exergonic processes (such as hydrolysis of ATP to ADP) is in tens of KJ/mole or few hundred meV (corresponding to 4-10 kT at room temperature). Thus, for bio-gating, energy to switch a physical system ON/OFF (i.e., gating) should be only few kT at room temperature requiring few electron charge. The challenge is to achieve the high sensitivity switching but avoid thermal noise. Central to the proposed research is to design, fabricate, and study a physical system composed of two dimensional (2D) network on 1D nanoparticle necklaces. Similar to a single nanoparticle, at cryogenic temperatures, the switching behavior is expected to be sensitive to charging by a single electron. In this project, we explore the possibility of observing single electron behavior at room temperature, and study coupling to living cell. As biology occurs in water, a goal is to extend the single electron behavior in aqueous media. The key challenge to obtain single electron behavior is to regulate the charge in the electrical double layer (EDL) formed on the necklace array.

FY 2012 HIGHLIGHTS

The most important result was demonstration of the single electron behavior in necklace array in aqueous media. The single electron behavior in 2D nanoparticle array studied theoretically and experimentally over a decade is shown to occur due to local charging of few nanoparticles by a single electron that poses a barrier to the (percolation) conduction path. This local charging, called the *quenched-charge-distribution* (QCD), is fixed. As the necklace array is immersed in aqueous media, QCD will be smeared due to the formation of the EDL. However, a strong single electron behavior is observed with a gain of ~130 fold as the charge in the EDL is gated. The observed electrochemical gating is an order of magnitude larger than that observed in graphene, carbon nanotube, and Si nanowire. By depositing green algae, light mediated bio-gating is observed. The photosynthesis process due to light stimulates the transport of CO_2 to stroma as HCO_3^- (mediated by RuBisCo enzyme) causing a raise in pH of the cell. As a result, the current in the necklace at fixed bias increases. The current gain due to bio-gating is consistent with the absorption spectrum of the chlorophyll.

Material Lessons from Biology: Single Crystal Synthesis and Polymorphism

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PROGRAM SCOPE

The nacre layer of the mollusk shell is a high-performance composite consisting of the calcium carbonate polymorph, aragonite, and a three-dimensional network of proteins that surround and inhabit each single crystal nacre tablet. From the BES energy-related materials viewpoint, the nacre layer offers a molecular “code” for three important processes: synthesis of single crystals, mesocrystal assembly, and polymorph stabilization. But to tap into this code, we need to understand what role(s) nacre proteins play in crystal building.

Recent studies now point the way to the non-classical pre-nucleation cluster (PNC) pathway as a means for proteins to control nucleation and crystal growth. What is so attractive about the PNC pathway is there are several stages, such as PNC formation, cluster assembly, and transformation, that are amenable to protein control. The question is, which stage(s) are controlled by which nacre proteins, and how is this control exerted?

The answer to this question comes from synthetic systems known as polymer-induced liquid precursors (PILP). PILPs are comprised of disordered polymers that can assemble PNCs, stabilize amorphous inorganic clusters, and permit transformation events. With the recent discovery by our laboratory that some nacre proteins behave like disordered polymers, we believe that the mollusk uses mechanisms similar to the PILP concept to create nacre biocomposites. Now, the challenge is to deduce which protein assemblies control what stages of aragonite nucleation, to determine if nacre protein assemblies are indeed “PILP-like” in character, and to establish the molecular forces that drive nacre protein behavior.

FY 2012 HIGHLIGHTS

We have established that biomineralization protein assemblies possess regions of mobility and disorder that are similar to isotropic motions in free, monomeric proteins. We believe that these are the “PILP-like” regions that are responsible for guiding stages of the PNC/ACC cluster pathway. We also determined that nacre protein sequences possess two traits that may be responsible for their assembly into matrix networks: intrinsically disordered sequences and amyloid-like aggregation-prone motifs. These features may be essential for forming protein matrices that can control the nucleation process, and may serve as building blocks for constructing new proteins that can control synthetic inorganic nucleation pathways.

Self-Assembly and Self-Replication of Novel Materials from Particles with Specific Recognition

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Funding:	$443,000

PROGRAM SCOPE

We plan to develop a new technology that harnesses the principles of self-assembly to build hybrid multi-functional materials with structures engineered at the nanoscale and the microscale. The key features of this new technology include the ability to place different functional elements of different material types (e.g., metals, semi-conductors, ceramics, polymers) precisely into pre-determined structures at the nano-micron scale. Although there are many technological advantages in nanoscale particles, structure and assembly, devices for energy collection, storage, and utilization are invariably macroscopic. Thus, there is a need for multiscale, probably hierarchical, assembly and several steps of mass production. The mass production of designed nanoscale structures is most efficiently accomplished by self-replication.

To be useful in fabrication, the process should have high fidelity in reproduction. However, what is essential to biology is to allow for occasional 'mistakes' that are also replicated, thereby setting the stage for evolution. At a later stage, we might want to take advantage of this ability of self-replicating systems to change under stress, in order to evolve better materials or devices.

FY 2012 HIGHLIGHTS

Since initial funding in the summer of 2012, we have made substantial progress in using novel specific and non-specific interactions for self-assembly and self-replication. In a recent paper, we presented the design rules for multiflavored, “polygamous particles” and showed that a single particle, DNA functionalized with many different "flavors," can recognize and bind specifically to many different partners. We investigated the cost of increasing the number of flavors in terms of the reduction in binding energy and melting temperature. We find that a single 2-mu m colloidal particle can bind to 40 different types of particles in an easily accessible time and temperature regime. (PNAS 109, 18731-18736, 2012).

We have also developed a new photolithography capable of patterning surfaces with DNA or with functionalites that can be bound to DNA. The technology is based on the photocycloaddition of cinnamate groups which are substitute for nucleosides in a DNA sticky end. With this technology, we can make designed patterns of different functionalization on flat and particle surfaces. We can also make permanent specific bonds between particles so that self assembly can employ both reversible and irreversible processes.

Programmed Nanomaterial Assemblies in Large Scales: Applications of Synthetic and Genetically-Engineered Peptides to Bridge Nano-Assemblies and Macro-Assemblies

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Funding:	$230,000

PROGRAM SCOPE

The current challenge of nanomaterial engineering is to assemble nano-building blocks into complex and larger-scale superstructures so that these nanomaterials with the unique property can be integrated as macroscale components in solar cells, microelectronics, metamaterials, catalysis, and sensors. Biomimetic assembly is an emerging technology in such pursuits since these organisms are efficient, inexpensive, and environmentally benign material factories allowing low temperature fabrication. The main objective in this proposal is to develop novel biomimetic material fabrication technology that can program directed assemblies of materials in the tailored shape and superstructure in large volumes (μm^3 - mm^3) from multi-nanomaterials, metal/semiconductor nanoparticles (NPs), and peptides. The overall hypothesis is that robust assemblies of synthetic or genetically-engineered peptides can form large-scale frames in targeted shapes by co-assembling NPs as joints, and these NPs are aligned in the resulting three-dimensional hybrid superlattices precisely in remarkable long-range order.

FY 2012 HIGHLIGHTS

In this term, a new three-dimensional reconfigurable assembly of diphenylalanine (DPA) peptides was generated by organizing them in three-dimensional metal-organic frameworks (MOFs). As a new application of biomaterials, this system was programmed to power autonomous motor actions without input energy. This new hybrid biomimetic motor system is powered by the release of DPA peptides from a MOF in a manner resembling the metabolization and production of resources in cells. Release of the stored peptides and their subsequent reconfiguration into hydrophobic assemblies creates a non-equilibrium condition by generating a large surface tension gradient, and the chemical energy generated by this process propels the MOF to swim like bacteria. Lessons learned from understanding how this motor operates could be used to design systems that sense, capture, and store or metabolize target chemicals and control the local environment of materials, which may lead to the development of energy efficient micro-robots.

Another three-dimensional peptide assembly was constructed by using functional metal NPs as joints. In this system, collagen-like peptides were assembled as frameworks with metal NP joints whose composite structure mimics bone tissues, and the mechanical strength of the resulting material is in the same order of natural bone tissues.

All of these results indicate that mimicking superior natural structures with flexible biomolecular systems allows one to design new artificial materials; understanding these materials leads to creation of new material designs which might exceed the properties of materials in nature.

Electrostatic Driven Self-Assembly Design of Functional Nanostructures

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

PROGRAM SCOPE

Viruses, organelles, and wall envelops of archaea organisms are examples of microcontainers of diverse shapes that perform specific biological functions. These closed crystalline structures are biological reactors that control various processes including metabolic flow even at very high salt concentrations, as with archaea organisms, or enhance the fixation of CO_2 in cyanobacteria, as with organelles called carboxysomes. They undergo transformation to perform specific functions, such as the conformational changes of viral capsids to release RNA inside cells. The mechanisms that lead to the emergence of various shapes at the mesoscale, as well as how these shape transformations couple to the functions of the nanocontainers, have been a mystery. Self-organized strong shells that undergo various geometrical transformations are of particular interest to nanotechnological applications, including imaging, catalysis, compartmentalization, and targeted delivery.

FY 2012 HIGHLIGHTS

By co-assembling oppositely charged lipids with variable degrees of ionization, we found a mechanism that leads to complex crystalline polyhedral shells and showed how their crystalline structures can be modified by externally modifying the surrounding electrolyte. That is, we found a way to regulate the shape of crystalline nano-containers. The buckled diverse geometries include fully faceted regular and irregular polyhedral, such as square and triangular shapes, or mixed Janus-like vesicles with faceted and curved domains that resemble cellular shapes and wall envelops of halophilic organisms. The symmetries of the resulting ionic nanocontainers were regulated by the pH values of the solution, which induced changes in their molecular structures. Transmission electron microscopy and in situ small- and wide- angle x-ray scattering demonstrated that these faceted ionic shells have hexagonal crystalline symmetry and that this symmetry makes them stable in closed shapes, and at high salt concentrations. Atomistic simulations revealed that the competition of physical interactions and charge-regulation induced transitions in crystalline states that translate in changes of shapes. The changes in packing symmetry translate in bilayer thickness changes that open the closed shapes (like a switch). The atomistic simulations demonstrated that the bilayer thickness and molecular packing are not homogeneous in the low symmetry closed shapes. The curved regions are less ordered and therefore would allow higher transport of molecules than the crystalline flat polyhedra faces. These discoveries shed light in the function of polyhedral cellular shells. Moreover, understanding the coupling of shape and composition through tuning chemical and physical interactions will enable the design of polyhedral structures for various applications including efficient nano-reactors to perform specific catalytic functions.

Nanoengineering of Complex Materials

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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 2012 HIGHLIGHTS

We have focused on self-assembly of peptide nanostructures and on the preparation of organic and hybrid organic-inorganic devices for solar cells. In one example, we have characterized the microstructure of macroscopic membranes formed by dynamic self-assembly between negatively charged polyelectrolytes with positively charged peptide amphiphiles. We find that variation of PA nanostructure morphology from spherical aggregates to cylindrical nanofibers allows membranes to act either as reservoirs for sustained release of cytotoxicity upon enzymatic degradation or as membranes with surface-bound cytotoxicity, respectively. For solar energy conversion, we have synthesized three-fold symmetric molecules and hairpin-shaped molecules with different chromophore moieties that self-assemble with fullerene acceptors to form the active layer in bulk heterojunction cells that are more efficient that non-assembled controls. In another example, we found that we can use both surface chemistry and molecular design to control the internal organization and orientation of electrodeposited hybrid organic-inorganic structures.

Multi-Responsive Polyelectrolyte Brush Interfaces: Coupling of Brush Nanostructures and Interfacial Dynamics

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Funding:	$150,000

PROGRAM SCOPE

The overall goal of this project is to, at a molecular level, understand and effectively control the dynamics of probe molecules at polyelectrolyte (PE) brush surfaces of tunable brush chain nanostructures and interfacial interactions under varied external stimuli. Specifically, the conformational nanostructures of PE brushes will be examined and optimized to consequently enhance interfacial molecular dynamics under varied solution pH, added salts and applied ac-electric fields. In this project, weak PE brushes of poly2-vinylpyridine (P2VP) will be mainly investigated with comparison to strong PE brushes of poly([2-methylacryloyloxyl ethyl] trimethylammonium chloride) (PMETAC), both of which will be grafted from a solid substrate via surface-initiated atom transfer radical polymerization (SI-ATRP) to precisely control their grafting density and thickness. Fluorescence correlation spectroscopy (FCS) with photon counting histogram (PCH) analysis will be used to determine the interfacial diffusive dynamics of single fluorescence molecules and local proton concentration at PE brush interfaces. With precisely controlled nanostructures of grafted PE brush thin films, the coupling of brush conformations and local counterion concentration of PE brushes in response to solution pH and added salts will be investigated. The interfacial dynamics of single probe molecules, neutral versus charged, on weak PE brush surfaces under nanoscaled ac-electric stimuli will be also examined to determine the optimal PE nanostructures and interfacial interaction to effectively enhance interfacial ion and molecular transport. The long-term goal is to establish a new paradigm in molecular design of polyelectrolyte based multi-responsive polymer thin films for lubrication, non-fouling coating, and efficient ion and molecular transport for energy storage and microfluidics applications.

FY 2012 HIGHLIGHTS

We have successfully utilized the ac-polarization effect to manipulate weak PE chains in dilute solution and tethered at surface to reversibly alter their structures between stretched and collapsed chain conformation and PE surface wettability by varied ac-frequency and voltage. Furthermore, we have examined the diffusive dynamics of single probe molecules on hard, soft and fluid polymeric thin films, and revealed that the molecular surface diffusion is determined not only by molecule-surface interaction, but also by the fluctuation dynamics of underlying surface coating.

A Hybrid Biological/Organic Half-Cell for Generating Dihydrogen

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PROGRAM SCOPE

The goal of this project is to develop a hybrid biological/organic photo-electrochemical half-cell that couples a photochemical module, Photosystem I (PSI), which captures and stores energy derived from sunlight, with a catalytic module, hydrogenase (H_2ase), which catalyzes H_2 evolution with an input of two electrons and two protons. The challenge is to deliver electrons from PSI to the H_2ase rapidly and at high quantum yield, thereby overcoming diffusion-based limits on electron transfer.

FY 2012 HIGHLIGHTS

The strategy to achieve this goal is to employ molecular wire technology to directly connect PS I with a catalyst. The wire serves to tether the photochemical module to the catalytic module at a fixed distance so that an electron can quantum mechanically tunnel between surface-located [4Fe-4S] clusters of PSI and a H_2ase at a rate faster than the competing charge recombination between P_{700}^{+} and F_B^{-}. To link the photochemical and catalytic modules, a short aliphatic or aromatic dithiol molecule forms a coordination bond with an exposed Fe of the F_B cluster of a PS I variant and with an exposed Fe of the distal [4Fe-4S] cluster of a H_2ase variant. This is practically achieved by changing a ligating Cys residue of the [4Fe-4S] cluster of each protein to a Gly, thereby exposing the Fe atom for chemical rescue by the added dithiolate-containing molecular wire. By optimizing the reaction conditions, the PSI—wire—[FeFe]-H_2ase construct evolves H_2 at a rate of 2850 µmoles mg Chl^{-1} h^{-1}, which is equivalent to an electron transfer throughput of 5700 µmoles mg Chl^{-1} h^{-1}, or 142 µmoles e^{-} PSI^{-1} s^{-1}. Putting this into perspective, cyanobacteria evolve O_2 at a rate of ~400 µmoles mg Chl^{-1} h^{-1}, which is equivalent to an electron transfer throughput of 1600 µmoles mg Chl^{-1} h^{-1}, or 49 e^{-} PSI^{-1} s^{-1}, assuming a PSI to PSII ratio of 1.8 as occurs in the cyanobacterium *Synechococcus* sp. PCC 7002. The greater than twofold 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. The modular design and highly flexible nature of these hybrid nanoconstructs, along with their stability, should allow for their incorporation into a variety of solar biofuel producing systems.

Enzyme-Controlled Mineralization in Biomimetic Microenvironments Formed by Aqueous Phase Separation and Giant Vesicles

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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 2012 HIGHLIGHTS

We have focused on performing calcium carbonate mineralization reactions in polymer-rich aqueous phase droplets that mimic the macromolecular crowding found in living organisms. The nonionic polymers used as macromolecular crowding reagents to mimic the intracellular environment do not substantially impact mineralization even when present at relatively high levels (30 wt%). Under conditions of phase separation, mineralization can be confined to one phase. We have begun exploring (1) the effect of polyanionic additives that interact with both calcium ions and calcium carbonate in these aqueous phase systems and (2) the presence of a semipermeable boundary layer consisting of anionic lipids. Methods have been developed to enable high-yield preparation of model mineralizing vesicles that are stable at the relatively high ionic strengths needed for mineralization. Work on these primitive models of mineralizing vesicles will continue in the next funding period.

Designing Smart, Responsive Communicating Microcapsules from Polymersomes

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PROGRAM SCOPE

The goal of this project is to design and understand responsive 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 that are released from a source capsule in response to light or change in pH. Much of the theory for interparticle communication and collective response has been developed by Dr. Anna Balazs at the University of Pittsburgh. It is our goal is to test these predictions experimentally. Central to our design are polymersomes—vesicles whose outer membrane is assembled from block-co-polymers. With the assistance of Dr. Daeyeon Lee (University of Pennsylvania), our collaborator on this project, 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 stimuli such as light. In these proposed experiments, we will release encapsulated nanoparticles from photo-sensitive polymersomes 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). By constructing spatial, ordered arrays of microcapsules using micro-contact printing, and by using nanoparticles and surfaces with tailored adhesiveness, we will make a direct test of the principles of collective smart particle motion predicted theoretically. The long-term impact of this work will be to develop autonomous, self-regulating motion of microcapsules that can communicate, mimicking biological activity.

FY 2012 HIGHLIGHTS

We have successfully made uniform microcapsules with controlled numbers of embedded nanoparticles and demonstrated that the particles can be released in response to optical illumination. Furthermore, we have shown that by tuning the adhesion of the substrate, we can make polymer vesicles that migrate over a uniformly adherent surface. In addition, we have shown that we can assemble a uniform population of biotinylated polymer vesicles made by microfluidic technologies in micropatterned arrays—made by microcontact printing, with micrometer spatial precision—and we can alter the spatial separation distance between the capsules over a wide range. Finally, we have shown that we can assemble vesicles from recombinant surfactant proteins, opening the possibility of embedding designer functionality into the capsule shell itself, such as protease cleavable domains that can facilitate dynamic responses in response to enzymes. This latter work was published in the Proceedings of the National Academy, USA. In the next period, we envision using our arrays to test the concepts of particle communication.

Modular Designed Protein Constructions for Solar Generated H_2 From Water

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Funding:	$245,000

PROGRAM SCOPE

Our long-term objective is to harness the energy of the sun for the production of inexpensive fuels and chemicals useful to mankind. We aim to achieve this with practical, design-flexible, stable, man-made proteins called *maquettes*. Maquette protein designs are informed by engineering and structural principles learnt from natural photochemical energy conversion and oxidoreductase catalysis. The work targets light capture to drive the splitting of water into bi-product O_2 and essential electrons and protons guided to sites of catalysis generating hydrogen. In the longer run, we look to develop catalysts for CO_2 and N_2 reduction for fuels and valuable carbon and nitrogen chemicals.

FY 2012 HIGHLIGHTS

In the past year, we have continued to develop maquette proteins that address the most challenging obstacles that stand in the way of efforts to develop solar fuel systems generally: sub-optimal energy conversion efficiency and damaging side-reactions, short-term stability of the supporting material, and working lifetime of the catalyst.

Electron tunneling calculations are showing that photochemical efficiencies observed in natural photosystems could be significantly improved with major effects on design, engineering, and construction of photochemical solar fuel systems. We are modeling natural photosystems to determine how much of the efficiency loss is naturally selected mechanisms to lower side-reaction damage. Current indications are that natural photosynthesis may be overcompensating and that maquettes faced with the same potential sources of damage can be made to higher standards of efficiency.

For five years, we have been exploring the single-chain four-α-helix protein as a practical material to support photochemical charge-separation; the past year has seen the work come to a promising conclusion. This protein demonstrates controllable stabilities including tetrapyrrole cofactors into the range typical of natural thermophilic proteins up to well above 70°C (most recent variant up to 95°C) and still assemble and function at ambient temperatures. The protein displays structural segments for separate functional development evidence by asymmetric positioning of a range of different light- and redox- active cofactors for a range of functions. With tetrapyrrole ligation, the protein assumes singular structure; we can make this general. The exterior of the protein can be changed extensively independent of the interior functions; this includes tolerance to very extensive alterations of net charge that can be patterned for functionally significant electrochemical control of cofactor electrochemistry. The same patterning offers a powerful device for assembly. And not least, this protein is bio-compatable; the maquette interacts with natural cytochrome c at physiological rates; and we have expressed the maquettes in *E.coli* equipped with redox and light active covalently-linked cofactors. We believe that the ultimate, and unique, value of our photochemical protein designs will be when they are integrated for function in natural cells.

Inducing Artificial Morphogenesis in Soft Synthetic Materials

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Funding:	$166,000

PROGRAM SCOPE

In biology, morphogenesis refers to the process that causes an organism to develop its shape. Our goal is to 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 systems we consider, 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, communicating microcapsules 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 studies are revealing a novel means of using light to organize and combine the individual pieces. By controlling the structure of these systems, we could achieve control over the functionality of the material.

FY 2012 HIGHLIGHTS

We used computational modeling to design a simple mechano-sensitive capsule that responds to mechanical deformation through a shape change that allows it to undergo self-sustained, directed movement. The capsules could serve as sensors for mechanical strain, indicating the presence of strain fields by their spontaneous motion and release of nanoparticles.

We also modeled polymer gels that contain spirobenzopyran (SP) chromophores and, thus, are photo-responsive. We showed that we can mold and remold the shape of the sample by illuminating the gel through a photomask and altering the opening in the mask. Our simulations also showed that the movement of a light source over these photo-responsive gels induces a well-defined expansion and contraction along the sample and results in its directed motion. By repeatedly moving the light source in a specific direction along the gel, we could drive samples of different shapes to undergo a net displacement in a well-defined manner. The ability to remotely manipulate both the shape of the sample and its directed motion is critical for driving multiple samples to recognize each other and ultimately dock to form various self-assembled structures.

Integrating Modeling and Experiments to Design Robust Self-Healing Materials

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Funding:	$380,000

PROGRAM SCOPE

Integrating expertise in computational modeling and chemical synthesis, our goal is to design and construct self-healing coatings, which are formed from cross-linked nanogels and nanoparticles. The inter-particle cross-linking involves bonds that can undergo a rapid degenerative exchange, allowing new bonds to be formed as old bonds are broken. Due to this behavior, the network of nanoparticles exhibits unique attributes: in response to mechanical deformation, the particles can quickly rearrange and reshuffle so that the mechanical integrity of the coating is maintained. In effect, this dynamic behavior prevents the coating from undergoing catastrophic failure. Since the coating remains intact, it protects the underlying material from the mechanical strain and severe damage. Thus, the research will yield new approaches for extending the sustainability and durability of manufactured components and systems.

FY 2012 HIGHLIGHTS

The Balazs and Matyjaszewski groups collaborated to develop a hybrid computational model for the behavior of networks of cross-linked polymer-grafted nanoparticles (PGNs). The individual nanoparticles are composed of a rigid 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 can form permanent or labile bonds, which lead to the formation of a “dual cross-linked” network. To capture these multi-scale interactions, our approach integrates the essential structural features of the polymer grafted nanoparticles, the interactions between the overlapping coronas, and the kinetics of bond formation and rupture between the reactive groups on the chain ends. Via this model, we determined the tensile properties of the dual cross-linked samples. We found that the mechanical behavior of the network can be tailored by altering the bond energies of the labile bonds, the fraction of permanent bonds in the network and the thickness of the polymer corona. Our model provides a powerful approach for predicting how critical features of the system affect the performance of cross-linked polymer-grafted nanoparticles and yields design rules for creating self-healing nanocomposites.

The experimental studies yielded a new method to control the self-healing of covalently cross-linked polymers by reshuffling thiuram disulfide moieties in air under visible light. We also established how changes in the network structure of chemical gels can be controlled by solvent quality through the photo-induced radical reshuffling reactions of trithiocarbonate units. Additionally, we reported on new self-healing polymer films based on thiol-disulfide exchange reactions and self-healing kinetics measured using atomic force microscopy.

Theoretical Research Program on Bio-Inspired Inorganic Hydrogen Generating Catalysts and Electrodes

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Funding:	$225,000

PROGRAM SCOPE

The overall goal of the program is the theoretical design of a model electrocatalytic or photo-electrocatalytic system for economical production of hydrogen from water via the hydrogen evolution reaction. The system we focus on is a FeS_2 (100) surface (the electrode) decorated with a cluster derived from the active site of the di-iron hydrogenase enzyme (the catalyst). The di-iron hydrogenases found in hydrogen-producing microorganisms have a turnover frequency of over 9000 H_2 molecules per second at room temperature, almost an order of magnitude faster than Pt. Their catalytically active site, the $[FeFe]_H$ cluster, could be an attractive candidate for a catalyst for hydrogen production from water by electro- or photo-catalysis. It is composed of abundant elements and is small enough to pack densely. The pyrite surface is chosen because its atomic structure is compatible with that of the hydrogenase active center and *a priori* suggests the possibility of stable linkage and easy electron transfer to the cluster.

It is known that di-iron hydrogenases are inactivated by oxygen and pyrite decomposes in the presence of oxygen and water. It is thus important to ascertain the sensitivity of the model catalyst/electrode complex to ambient oxygen present in practical hydrogen-production contexts. If the complex also proves to be oxygen sensitive, an additional goal is to design a protective (nano-)structure which inhibits the attack of the clusters and the exposed FeS_2 sites by dissolved O_2.

FY 2012 HIGHLIGHTS

In earlier work, we designed a stable, efficient catalyst/electrode complex, $[FeFe]_P/FeS_2$, which produces hydrogen from acidified water with a free-energy barrier of less than 8.2 kcal/mol in room temperature simulations. The $[FeFe]_P$ catalyst could be an efficient, inexpensive hydrogen producer if it avoids the O_2 poisoning of the hydrogenase active center. To address this, in 2012 we investigated the binding of solvated oxygen to $[FeFe]_P/FeS_2$ and its subsequent reaction with the cluster in water via density-functional theory calculations and Car-Parrinello molecular-dynamic simulations. We found the cluster to be oxygen tolerant, reducing to water any oxygen it binds, and surviving without structural change for times far longer than those of practical concern.

An Investigation Into the Effects of Interface Stress and Interfacial Arrangement on Temperature Dependent Thermal Properties of a Biological and a Biomimetic Material

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Funding:	$160,000

PROGRAM SCOPE

The proposed research is based on a hypothesis that in synthetic materials with biomimetic morphology, thermal conductivity, *k*, (how fast heat is carried away) and thermal diffusivity, *D*, (how fast a material's temperature rises: proportional to the ratio of *k* and heat capacity) can be engineered to be either significantly low or significantly high based on a combination of chosen interface orientation and interfacial arrangement in comparison to conventional material microstructures with the same phases and phase volume fractions. Once obtained, such values can remain constant as a function of temperature change (positive or negative) as well as external stress change to enable a predictive deployment of biomimetic material architectures in applications involving thermal cycling or high thermal gradients, such as thermal management systems, solar thermal absorbers, energy applications involving laser heating, etc. The hypothesis is based on recent analyses of thermal conduction and thermal diffusivity in a nacre type Si-Ge biomimetic material morphology by the principal investigator. Analyses will be performed by combining quantum simulations based on density functional theory (DFT) and classical atomistic simulations based on non-equilibrium molecular dynamics (NEMD) with experiments.

The objectives focus on (1) investigating thermal conduction as well as measuring heat capacity contribution of varied orientations of tropocollagen (TC)-hydroxyapatite (HAP) and Si-Ge interfaces using quantum mechanical simulations based on DFT at the nanoscopic length scale (~10 nm) as a function of temperature change and at different levels of applied stress; (2) investigating correlation of interfacial thermal conduction and heat capacity contribution at quantum simulation length scale to thermal conductivity and heat capacity in varied biomimetic and conventional (e.g., nanocrystalline microstructure, superlattice etc.) microstructures of Si-Ge and TC-HAP using classical atomistic simulations based on NEMD (~10 nm-200 nm); and (3) validation and correlation of the classical and quantum simulation results with experimental measurements of thermal conductivity as a function of applied stress in photo lithographically processed Si-Ge biomimetic architectures (http://www.noeltech.com/index.html) and available biological samples of TC-HAP [mainly bone samples as well as TC-HAP biomaterial samples available commercially (http://www.synthes.com/Pages/default.aspx)].

FY 2012 HIGHLIGHTS

The project was initiated in September 2012. One PhD student, Yang Zhang, has been hired to work on the experimental component of the proposed work. The experimental work is focusing on Si-Ge superlattice biomimetic materials and bone bio-samples to perform nanoscale to micron scale thermal diffusivity and thermal conduction measurements. Dr. Tomar is focusing on computational aspects to identify the setup of quantum mechanical and classical molecular simulations in line with experimental investigations.

Engineering the Interface between Inorganic Materials and Cells

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PROGRAM SCOPE

This proposal is motivated by the goal of interfacing biological and non-biological components to create "living materials." A recent report from the Basic Energy Sciences Advisory Committee noted that building functional interfaces between the living and nonliving may make it possible to harness the unmatched capabilities of living systems and apply them to our own purposes. Indeed, the adaptation of cells to DOE goals – for example biosensing, environmental bioremediation, and energy harvesting – will require cells to function outside of their native environment, as components of hybrid cell-material systems. Since most interfaces of cells with inorganic materials are unnatural, engineering of both the inorganic surface and the cell are required to ensure optimal cellular behavior. However, the majority of prior studies have focused on engineering the surface chemistry of the material. In contrast, our proposed work will focus on cellular engineering efforts to integrate cells with pristine inorganic materials and to endow cells with the capability to respond to novel signals. Specifically, we will investigate a cellular engineering approach for promoting the adhesion and survival of neurons on inorganic surfaces. We will explore two complementary approaches for engineering neurons to respond to light as a signal. We will also engineer a light amplification "circuit" inside a neuron. While our proposed cellular engineering efforts are not focused on a specific application, one downstream target application involves the development of biosensors that use cells as the detection element and inorganic structures for signal transduction and display. However, our general cellular-engineering-based approaches to promote cell viability and function on inorganic materials will likely be broadly applicable to DOE mission goals.

FY 2012 HIGHLIGHTS

We have developed an optogenetic method, based on *A. thaliana* Cry2, for rapid and reversible protein oligomerization in response to blue light. We demonstrated the ability to use this method to channel the light input into several defined signaling pathways. We have also demonstrated the ability to use light to control basic cellular processes. We are continuing our cellular engineering efforts to integrate cells with materials and devices.

Optimizing Immobilized Enzyme Performance in Cell-Free Environments to Produce Liquid Fuels

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Funding: $145,000

PROGRAM SCOPE

The overall goal of the research is to produce alcohol (butanol) via a cell-free in vitro two-enzyme system while simultaneously removing the alcohol to reduce feed-back inhibition. We focus on the bioconversion of acids to aldehydes to butanol. While this enzymatic route offers great promise and excellent selectivity for the production of biofuels, enzymes exhibit slow kinetics, low volume capacity in solution, and product feedback inhibition. These limitations have to be overcome so that biofuels can be produced economically. Directed evolution will be used here to address these limitations. The enzymes, synthesized via recombinant DNA technology, will be immobilized on a solid substrate in order to stabilize them and allow the product to continuously be removed while retaining catalyst. This cell-free enzyme system will be coupled with a membrane process to continuously remove the desired butanol.

FY 2012 HIGHLIGHTS

To date, we have determined an effective immobilization strategy with a model enzyme beta-galactosidase and, recently, with alcohol dehydrogenase (ADH), one of our two enzymes for butanol production. We have also used error-prone PCR and found stable ADH mutants to temperature and high levels of butanol. We have cloned, over-produced, and purified both critical enzymes, ADH and keto-acid decarboxylase (KdcA). The model immobilized enzyme, beta-galactosidase, was chosen to determine the optimal substrate geometry (flat, convex, or concave). Preliminary data indicates that crowding and orientation of the immobilized enzymes have a large effect on enzyme kinetics. Serial reactions of immobilized KdcA and ADH to produce butanol *ex-vivo* was also evaluated in solution and bound to substrates. Finally, The effect of iso-butanol on the kinetics of the enzymes, both in solution and immobilized, was evaluated. In the next period, we plan to continue the error-prone PCR with KdcA to seek stable enzymes to both temperature and butanol concentrations, and then combine the two enzymes into a single reactor to produce butanol.

Biopolymers Containing Unnatural Building Blocks

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Funding: $500,000

PROGRAM SCOPE

This project is aimed at the use of genetically encoded unnatural amino acids with novel structures and properties to engineer biomolecules with useful materials properties.

FY 2012 HIGHLIGHTS

We have made significant progress on several fronts: (1) We have used metal ion binding amino acids to engineer a metal ion binding site into the protein zif268. We have also used the same amino acid to evolve selective metal ion binding peptides. This work may provide a general approach to the creation of metalloproteins with novel catalytic or structural properties. (2) We have genetically encoded an amino acid that can photoinitiate atom transfer radical polymerization reactions. We are currently attempting to use this amino acid to polymerize monomers in phage capsids to generate "nano-molded" polymers. (3) We have developed a new method to create sensor assays using amino acids with orthogonal chemical reactivity. This work may allow the development of more efficient sensors by giving greater control over the orientation of immobilized biomolecules. (4) We have generated a new orthogonal tRNA/aminoacyl-tRNA synthetase pair as a next step toward generating a new class of templated condensation polymers with exquisite control of monomer sequence and length.

Using *In vitro* Maturation and Cell-free Expression to Explore [FeFe] Hydrogenase Activation and Protein Scaffolding Requirements

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Funding: $265,000

PROGRAM SCOPE

The goal of this project is to elucidate the assembly mechanisms and the structural requirements for [FeFe] hydrogenases so that essential synthetic, geometric, and catalytic principles can be replicated to develop durable and highly productive inorganic catalysts for the efficient production of hydrogen from electricity and from sunlight. In parallel, we aim to use the knowledge gained to design, produce, and test new hydrogenases that are functionally superior to naturally isolated enzymes.

In this funding period, we seek to develop a fully defined in vitro hydrogenase maturation system to elucidate the substrates and mechanisms for assembly and maturation of the 6Fe-6S active site in [FeFe] hydrogenases. The underlying hypothesis is that *in vitro* hydrogenase maturation processes can sufficiently mimic *in vivo* mechanisms for definitive evaluation of fundamental assembly hypotheses. We also seek to isolate and evaluate a large family of [FeFe] hydrogenase mutants that retain catalytic function while being singly or multiply modified near the active site and proximal Fe-S center to gain extensive understanding of enzyme function and scaffolding requirements. The underlying hypothesis is that analyzing the structural requirements of the polypeptide scaffolding supporting the key Fe-S centers will provide insights into structure-function relationships that will eventually enable the design and synthesis of effective biomimetic hydrogenases.

FY 2012 HIGHLIGHTS

In 2012, we reported improvements to the *in vitro* [FeFe] hydrogenase maturation system that demonstrated catalytic function for the maturases. However, full activation still required an *E.coli* cell extract. To determine if the *isc* iron-sulfur cluster producing enzymes could replace the extract, each of the 6 *isc* proteins was cloned, expressed, and purified; and its activity was confirmed. Unfortunately, these purified proteins only provided a very small benefit and did not support full hydrogenase activation. We now observe that specific fractions of the cell extract enable full activation; and these are enabling a search for the unknown, active component(s). We produced a library of hydrogenase mutants with amino acid replacements at all sites surrounding the H-cluster active site and proximal Fe-S cluster. An initial analysis of alanine replacements indicated that more than 90% of the mutants retained activity suggesting surprising plasticity and supporting the study strategy. A high throughput hydrogen evolution assay system is now being developed to facilitate full library evaluation for hydrogen production activity. This uses sequential digital images of a titanium dioxide/palladium sensor plate that is sealed over a 96-well reaction plate. This analysis is conducted in a hydrogen-free glove box. In addition, we have developed hydrogenase mutants designed to individually “knock-out” each of the electron conducting Fe-S centers. These mutants suggest that electrons delivered by ferredoxin enter the enzyme only at the distal 4Fe-4S cluster while electrons delivered by methyl viologen can enter at that site, at the 2FE-2S cluster or, to a small extent, directly into the H-cluster. These hydrogenase mutants are now being more fully evaluated using EPR spectroscopy. In addition, a new report has just been accepted by *Biochemistry* to show that the cell-free maturation system mentioned above can selectively introduce ^{57}Fe into the active site.

Functional, Hierarchical Colloidal Liquid Crystal Gels and Liquid Crystal Elastomer Nanocomposites

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Students:	0 Postdoctoral Fellow(s), 3 Graduate(s), 0 Undergraduate(s)
Funding:	$250,000

PROGRAM SCOPE

Microparticles dispersed in low molecular weight liquid crystals (LMWLCs) generate topological defects within the LC phase. Such defects formed in the LC can mediate inter-particle interactions that lead to the formation of particle clusters or chains. Less is known about the behavior of nanoparticles in LCs. Efforts at the UW-Madison have sought to develop an understanding of nanoparticle-LC interactions, the way in which such particles alter LC structure (leading to formation of gels), and the way in which LC structure (for example in LC elastomers) can influence nanoparticle interactions.

FY 2012 HIGHLIGHTS

A key accomplishment of the UW-Madison research has been to show that, by controlling the size of particles and their chemistry, one can alter LC-mediated interactions between them over a range of energies that encompasses several decades of magnitude in kT. A second achievement has been the demonstration that droplets of LMWLCs can be used to manipulate the defects that arise in the LC, thereby providing a platform for precise control of LC-mediated nanoparticle interactions. That concept has been taken one step further and used in the context of a molecular model to demonstrate that nanoparticles at the interface of LC droplets adopt highly ordered structures, whose morphology is dictated by particle size, concentration, and the strength and type of interaction with the liquid crystal. The phases that arise at such interfaces are reminiscent of those seen in block polymers and include lamellar, spherical, and bicontinuous structures. A third achievement of the UW-Madison research has been the demonstration that, in the bulk, nanoparticles dispersed in an LMWLC can be used to gel the LC matrix and provide a rigidity to the samples that is of interest to future applications of these materials.

A parallel research direction has examined the structure and mechanical response of nanoparticle-laden LC elastomers, where LMWLC molecules are crosslinked to add structural integrity to the material. A newly proposed molecular model has been used to reveal a polydomain texture in LC elastomers. As a uniaxial stress is applied, the system initially remains in a polydomain state; but individual domains rotate about themselves in order to accommodate the applied external stress at a local level. Above a critical, threshold value, the system exhibits a transition from a polydomain to a monodomain state. The monodomain system becomes uniformly nematic. The corresponding stress-strain curves for the model LCE are consistent with those observed in experiments. It is found that nanoparticle addition does not influence the overall soft-elasticity behavior of the LCE. However, at a local level, the nanoparticles induce a strain in nearby mesogens that alters their orientation significantly.

Optical and Electro-Optic Modulation of Biomimetically-Functionalized Nanotubes

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Funding:	$285,000

PROGRAM SCOPE

Light triggered changes in biological molecules which enable various functions such as vision, photosynthesis, and heliotropism (or solar tracking) have long inspired materials chemists to mimmic these phenomenon to create new functional materials and devices. The ability to detect and translate the conformational changes in the small molecule retinal into the macroscopic effect of vision exemplifies a very powerful and elegant approach to the design of new functional materials. Carbon nanotubes, with their exceptional electrical conductivity, robustness, and small size, have attracted much interest as possible nanoscale replacements for inorganic semiconductors. Our goal is to combine the best of these two worlds to design a nanotube/chromophore hybrid material. Here the nanotubes function as a probe of molecular transformation and also as a medium to translate the optical modulation of elecro-optic properties into useful devices. Our proposed research is inspired by the biological process of vision and focusses on using a range of dipolar chromophores based on azo-benzene structure which undergo reversible wavelength dependent cis-trans isomerization. These chromopores are photochemically stable, can be reversibly switched 10^5 to 10^6 cycles before fatigue, and can be chemically tuned. We aim to answer key questions such as *does the binding of the chromophore to the nanotube modify the chemical response? Is the chromophore optical absorption modified by the nanotube?* and *Can we detect a single molecular transformation event by monitoring the nanotube conductance?* One can reasonably envision a future functionalized-nanotube-based electro-optics with strong electro-optic coupling (due to well-engineered chemical functionalization, our proposed work), uniform response (due to single chirality, a technology being rapidly developed by other groups), and high-speed (due to the intrinsic, and by now well demonstrated, high mobility of carbon nanotubes).

FY 2012 HIGHLIGHTS

We have (1) completed the synthesis of a series of azobenzene based dyes; (2) built a setup to probe the electro-optical characteristics of the interface under high vacuum conditions; (3) made progress on the design and synthesis of new conjugated polymers, which have the dual function of IR responsiveness and switchability in the UV range; (4) developed a parallel effort on graphene (*Nano Letters* 2012. *12*, 182–187); (5) completed solution characterization of the nanotube-chromophore hybrids to understand the nature of chemical and electronic coupling (*ACS Nano* 2011. *5*, 7767-7774); (6) initiated theoretical effort to understand the observed characteristics; and (7) developed second harmonic generation tools to probe the molecular orientation on carbon based materials (APL, 2012 in revision).

DOE National Laboratories

Bioinspired Materials	
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Students:	3 Postdoctoral Fellow(s), 4 Graduate(s), 3 Undergraduate(s)
Funding:	$900,000

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 2012 HIGHLIGHTS

Building on our past efforts, we have expanded synthesis of complex magnetic nanoparticles to patterned surfaces. This permits control over formation and placement of magnetic nanocrystals on a surface, allowing for interesting magnetic properties with chains of crystals. We are elucidating the role of the mineralization protein Mms6 from magnetotactic bacteria. We have shown that Mms6 binds iron very tightly stoichiometrically and then binds large amounts of iron at lower affinity to a limiting amount of ~18:1 (iron:protein). Even though the bacteria normally produce either magnetite (Fe_3O_4) or greigite (Fe_3S_4), we have synthesized more complex magnetic nanoparticles containing manganese and gadolinium using the same proteins. We are currently working on comprehensive characterization of magnetic properties of these complex ferrite systems. We are building all-atom molecular dynamics simulations of the C21 peptide using a starting structure based on solution NMR data. We also continue working with a variety of magnetotactic bacteria, probing the incorporation of dopant cations into the magnetosome magnetite crystal.

We have used similar bioinspired approaches to create mesoporous zirconia with large surface areas and enhanced thermal stability using mineralization proteins such as lysozyme coupled to self-assembling block copolymers. In addition to chemical conjugation between the proteins and the polymer templates, the use of complementary DNA strands confers additional reversibility, especially on surfaces. This work is being guided by the computational studies of DNA programmed self-assembly. The simulations have also been focused on the self-assembly of templates in the presence of anisotropic nanostructures such as nanorods.

Emergent Atomic and Magnetic Structures

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Funding:	$500,000

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 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. Bio-inspired synthetic routes offer room-temperature pathways to a variety of magnetic nanostructures having shapes and sizes not realizable via conventional inorganic chemical techniques. We work on gaining a better understanding of how the assembly of biomacrolecules dictates nanoparticle formation and functional properties, and our research is motivated, in large, by the findings of the Bio-Inspired Materials FWP at Ames Laboratory. We use magnetite nanoparticles biomineralized by the magnetotactic bacteria, utilizing these tiny magnets to align themselves along the Earth's magnetic field, as a model system.

FY 2012 HIGHLIGHTS

A new group of bacteria, discovered by the group of our collaborator, Dennis Bazylinski, in Death Valley's Badwater Basin, was shown to make nanoparticles of both magnetite (Fe_3O_4) and greigite (Fe_3S_4), whereas typical magnetotactic bacteria do not make both minerals. The discovery dispels that notion that greigite-producing bacteria live only in marine environments. This is also the first successfully isolated, grown, and gene-sequenced sulfur-reducing magnetotactic bacterium. The researchers found two different genetic clusters related to magnet formation, suggesting that one is responsible for making magnetite and the other greigite. The discovery will help provide insight on the chemical conditions under which greigite is formed, which could be important for figuring out how to mass produce these magnetic nanocrystals for nano- and biotechnology applications.

The work on characterization of novel microorganisms shown to biomineralize inorganic matter resulted in an identification of new strictly anaerobic *Lachnospiraceae* bacterium, representing a novel genus and species, which was isolated from the human subgingival dental plaque. The oral cavity is a major gateway to the human body and better understanding these types of microorganisms is of obvious interest. Comprehensive characterization of biomineralization processes in anaerobic bacteria might provide new clues on chemical processes associated with formation of various inorganic biominerals, which, in turn, could lead to their synthesis *in-vitro*.

We have initiated working with the liquid cell TEM holder platform and identified the key parameters for monitoring the juvenile amorphous nanoparticles and a timeline of their crystallization, and established the most suitable imaging and analytical modes. As a part of our continuous research effort in magnetotactic bacteria, we successfully tested *in-vivo* imaging of several bacterial strands utilizing the liquid cell TEM holder platform.

Dynamics of Active Self-Assembled Materials

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Funding:	$1,006,000

PROGRAM SCOPE

Self-assembly, a natural tendency of simple building blocks to organize into complex architectures is a unique opportunity for materials science. The in-depth understanding of self-assembly paves the way for the design of tailored smart materials for emerging energy technologies, such as materials that can self-regulate porosity, strength, water or air resistance, viscosity, or conductivity. However, self-assembled materials pose a formidable challenge, as they are intrinsically complex, with often hierarchical organization occurring on many nested length and time scales. Our approach is a combination of in-depth theoretical and experimental studies of the dynamics of active self-assembled material for the purpose of control, and the prediction and design of novel bio-inspired materials for emerging energy applications.

In the past three years, our program yielded discoveries of self-assembled magnetic swimmers, drastic reduction of viscosity in suspensions of swimming bacteria, extraction of useful energy from chaotic movement of swimmers, and magnetic manipulation of self-assembled colloidal robots. For all these model systems, we have developed theoretical descriptions leading to the prediction and control of emergent self-assembled structures.

FY 2012 HIGHLIGHTS

Biological cells are capable of sensing mechanical cues and responding to these signals by undergoing morphological changes and directed motion. A significant challenge is creating cell-like objects that can translate mechanical stimuli into analogous behavior. We used computational modeling to design a simple mechanosensitive ‘‘cell’’ that responds to mechanical deformation through a shape change that allows it to undergo self-sustained, directed movement. Our cellular object is formed from a nanoparticle-filled microcapsule that is located on an adhesive substrate in solution. In response to a locally applied force, the deformed capsule releases nanoparticles that bind to the surface and dynamically create adhesion gradients. Due to the self-generated gradients, the capsule moves autonomously from regions of less adhesion to greater adhesion. During the capsule’s motion, new nanoparticles are released that both sustain and propagate the adhesion gradients and thus, the capsule sustains autonomous movement along its path (until it is depleted of nanoparticles). The self-sustained motion occurs only if the permeability of the capsule’s shell depends on mechanical deformation. Our findings can facilitate the fabrication of self-healing devices that are powered by the autonomous movement of microscopic synthetic cells. Additionally, the capsules could serve as sensors for mechanical strain, indicating the presence of strain fields by their spontaneous motion and release of nanoparticles; the latter behavior could be exploited in the fabrication of self-healing materials.

Nanostructured Biocomposite Materials for Energy Transduction

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Funding: $650,000

PROGRAM SCOPE

The objective of this project is the design, synthesis, and characterization of nanostructured biocomposite materials that exploit the native capabilities of biological molecules to store and transduce energy. A major research thrust in this work is the development of biologically-inspired synthetic soft materials that stabilize, organize, and regulate the activity of a wide variety of proteins. The work encompasses the design and synthesis of small organic molecules (e.g., amphiphiles, monomers) that constitute the fundamental building blocks used to fabricate these materials. The molecules are tailorable permitting re-programming their spontaneous organization into a variety of nanostructures. Chemical moieties are also added to allow for capture of the self-assembled architectures in a durable form by polymerization and/or crosslinking, rendering the materials environmentally stable and mechanically durable.

A second thrust of the program is centered on synthetic modification of the soft materials to allow for successful biotic-abiotic functional integration. The seamless integration of functional interfaces for connecting protein input and output (e.g., light-generated electron flow) to enable connection of the nanoscopically organized biomolecules to the macroscopic world is an important requirement if the resultant composites are to find application in energy-related technologies. Photonic connections will be achieved by co-integration of natural and artificial light-harvesting units, while electronic connections are achieved by formation of nanoparticle-polymer composites or by inclusion of a polymerizable p-conjugated moiety.

FY 2012 HIGHLIGHTS

Our efforts were directed at developing soft electronic materials for interfacing biological molecules to traditional inorganic electronic conductors. The specific achievements are highlighted below:

Post-polymerization radical bromination of a liquid-crystalline poly(ionic liquid) that selectively introduces a reactive bromo-group onto a polyalkylthiophene backbone was achieved. Cyclic voltammetry confirmed spectroscopic findings that the bromination yielded a stable *p*-doped polymer. Electrochemical studies also show that introduction of the electron-withdrawing bromine enhances *n*-doping. The installed bromine is susceptible to nucleophilic displacement permitting the covalent attachment of other functional molecules.

Glucose oxidase was physisorbed on an ionic liquid-derived polymer containing internally organized columns of Au nanoparticles and exhibited direct electron transfer and bioelectrocatalytic properties towards the oxidation of glucose.

Soft-Matter Physics: Directed Self-Assembly of Soft-Matter and Biomolecular Materials

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Funding:	$931,531

PROGRAM SCOPE

The goal of this project is to understand the effects of nanoscale confinement and the role of self-assembly in soft and biomolecular materials through the use of patterned templates and well-defined interfaces. Patterned templates are fabricated in collaborations with Chuck Black (CFN/BNL) using e-beam patterning—lateral features sizes as small as 40 nm—whereas the chemical patterns are fabricated using an AFM based, nanoscale oxidative lithography—lateral features of 40 nm and above. Well-defined interfaces encompass liquid/vapor, liquid/liquid, and liquid/solid interfaces. We use synchrotron x-ray scattering, scanning probe, and optical microscopy techniques to study the confinement induced structure of complex fluids, simple liquids, macromolecular assemblies, liquid crystals, polymers, organic photovoltaic materials, and biomolecular materials. An important aspect of our research is to understand the filling, shape, and stability of liquids on nanopatterned surfaces. The group has a major effort to investigate the assembly of nanoparticles, including virus particles, at lipid interfaces and surface freezing—the simplest type of self-assembly—of organic molecules at the vapor, solid, and liquid interfaces. The group works closely with theorists—aided by an annual summer workshop—to test our results with microscopic theory and simulations. To carry out these objectives, the Soft Matter Group develops instrumentation, and maintains and operates a beamline at the National Synchrotron Light Source (NSLS). We play an important leadership role in two beamlines at NSLS II.

FY 2012 HIGHLIGHTS

We have elucidated the stability of ultrathin liquid films against dewetting by studying a model system composed of a simple, volatile liquid (octane) wetting a chemically patterned substrate. The patterns are composed of periodic arrays of alternating completely and partially wettable nanostripes. The film morphology was recorded using noncontact AFM while varying the film thickness with sub-nanometer resolution (through precise control of the liquid undersaturation). We find that the liquid film becomes unstable and dewets the partially wettable nanostripes below a critical thickness proportional to the width of the stripes. This behavior was modeled precisely by accounting quantitatively for the long-range, attractive and short-range, repulsive molecular interactions between the liquid and the substrate.

Molecularly thin alkane layers, deposited at the vapor interfaces of an aqueous solution, were used to facilitate the 2D assembly of TYMV, an icosahedral virus. The assembly is driven by the hydrophobic interactions between the interface and the non-polar patches of the virus surface. In-situ grazing-incidence small-angle x-ray scattering measurements demonstrated that the assembly resulted in dense 2D arrays with only short-range order. This is in contrast to the case of the electrostatics-driven 2D assembly of TYMV on cationic lipid monolayers, which induced 2D crystallization under the same solution conditions. The result points to the importance of well-defined interfacial particle orientation in generating long-range order.

Directed Organization of Functional Materials at Inorganic-Macromolecular Interfaces

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Funding:	$900,000

PROGRAM SCOPE

The purpose of this project is to develop a quantitative physical picture of macromolecular organization and its relationship to function, and use macromolecular organization to derive new functionality. The research is divided into three subtasks: (1) fabrication of bio-nanoelectronic devices based on lipid-protein layers assembled on “1D” nanowires, (2) creation of artificial light harvesting complexes using virus-DNA origami arrays on 2D chemical templates, and (3) determining the mechanistic controls on formation of extended 2D macromolecular structures in which conformational transformations are an inherent feature of assembly and multiple order parameters evolve on distinct timescales, using two self-organizing systems—S-layer tetramers and collagen triple helices. Through these subtasks, we will utilize in situ characterization tools and simulations to develop an understanding of assembly pathways and dynamics, and relate organization to function. Our goals are to determine the role of interface structure on organization dynamics; explore the impact of cooperativity arising from adsorbate-adsorbate and adsorbate-substrate interactions; quantify the interfacial energies and kinetic barriers that drive organization; determine the effect of competing timescales for condensation, ordering, and conformational transformations on assembly pathways and dynamics; and use organization to derive new functionality and explore the correlation between these two phenomena.

FY 2012 HIGHLIGHTS

In situ characterization of individual nanowires: We are developing fundamental approaches that use templated self-assembly to make functional connections between biomolecules and nanomaterials. With scanning transmission x-ray microscopy (STXM), we probed the orientation and order of lipid molecules by examining the polarization dependence of the C 1s absorption spectra measured on individual phospholipid coated nanowires. Further, as we can adjust the diameter of the SiNWs, we can parameterize the substrate curvature and its effect on the orientation and relative molecular packing of the lipid bilayer.

Describing molecular bonding: We developed and experimentally verified a model for comprehensive description of bond formation and rupture, that resolves inconsistencies in current interpretations of rupture force spectra. The standard model for interpreting non-linear single molecule rupture force spectra arbitrarily assumes multiple barriers to bond rupture, resulting in non-physical bond parameters and inconsistent interpretation. Our model shows that this nonlinearity emerges from reforming of a single bond or from asynchronized rupture of multiple individual bonds. In this case, spectra non-linearity arises naturally as the system transitions from a near-equilibrium regime to a kinetic regime. Our simple, self-consistent model is expected to become the standard for analysis of the single molecule bond rupture experiments.

Bioelectronics: We have continued to build and characterize assemblies that combine functional membrane proteins with 1D bilayer electronic architectures. We demonstrated a system that incorporated photoactivated rhodopsin proton pumps into a bioelectronic FET device.

Molecular Nanocomposites

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Funding:	$80,000

PROGRAM SCOPE

The goal of this program is to establish the key scientific principles needed to design and fabricate molecular nanocomposite materials that integrate functional molecular and/or biomolecular components with rigid nanostructured inorganic architectures. Our current efforts are focused on understanding interfacial issues between encapsulated nanomaterials and the surrounding matrix. This understanding will provide the fundamental knowledge needed to optimize material functions in the matrix. Such studies will lead to new techniques for the characterization and preparation of functional composite materials with potential applications in molecular and biomolecular sensing, as well as next generation photovoltaic materials.

The key LANL investigator is Andrew M. Dattelbaum, who works in collaboration with a larger research team at Sandia National Laboratories (Albuquerque) led by Jeff Brinker.

FY 2012 HIGHLIGHTS

A general challenge in generating functional materials from nanoscale components is integrating them into useful composites that retain or enhance the properties of interest. We have demonstrated an innovative approach to obtain highly fluorescent solution-free SWNT-silica aerogels, which provides access to novel photophysical properties. We observed strongly blue-shifted spectral features, revelation of new diameter-dependent gas-phase adsorption phenomena, and a significant increase (~ 3× that at room-T) in photoluminescence intensities at croyogenic temperatures that all indicate greatly reduced SWNT-matrix interactions consistent with the SWNTs experiencing a surfactant-free environment. The results demonstrate that this solid-sate nanomaterial will play an important role in further revealing the true intrinsic SWNT chemical and photophysical behaviors and represent for the first time a promising new solution- and surfactant-free material for advancing SWNT applications in sensing, photonics, and optoelectronics (Ref: *ACS Nano* 2011, 5, 6686-94, DOI: 10.1021/nn202225k).

We have begun the encapsulation of more complex bioassemblies in silica using a novel silica encapsulation process. In particular, we are optimizing the sol-gel processing conditions needed to encapsulate retina harvested from frog. We have successfully encapsulated retina in silica and electrically observed its function under light stimulation for more than 12 hours. The silica condensation process and conditions were critical to realizing the encapsulation of functional retina in silica. Future work will be focused on understanding the interactions between the silica matrix and retina to optimize its functional lifetime, which could be a significant advance in our understanding of bio-interactions with inorganic materials.

Molecularly Engineered Biomimetric Nanoassemblies

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Students:	6 Postdoctoral Fellow(s), 2 Graduate(s), 6 Undergraduate(s)
Funding:	$730,000

PROGRAM SCOPE

Our goal is to develop new materials for energy transduction inspired by the assemblies found in Nature. Nature utilizes a broad set of assembly scaffolds and strategies to organize inorganic and organic chromophores leading to materials with controlled structure, emergent properties, and adaptive behavior that span length scales from the molecular to the mesoscopic. We are developing nanoscale materials with adaptive and tunable responses that can be integrated into complex architectures using self- and biologically-assisted assembly methods. Specifically, we are developing membrane-based assemblies of synthetic nanoscale materials that are capable of light-driven charge separation and assemblies of novel nanomaterial-based chromophores that can function in energy harvesting arenas. Our work is divided into two major directions, each aimed at different functional aspects of material assemblies. In the first, we target the development of complex assemblies with photo-induced charge separation performance. In the second, we develop assemblies of metal nanoclusters that enable the control of electromagnetic fields or light-harvesting.

FY 2012 HIGHLIGHTS

Toward developing materials capable of photo-induced charge separation, we have demonstrated the synthesis and characterization of conjugated oligomers and their self-assemblies. These conjugated oligomers exhibit tailored optical and electronic properties, and can be functionalized for facile attachment to lipids, self-assembling proteins, and to DNA (creating conjugated nucleic acids that can utilize DNA for assembly of electronic materials). Toward inclusion of these materials within lipid assemblies, we have developed tethered supported lipid bilayers to define lateral structure and functionality within membrane assemblies. Through neutron reflectivity studies, we find that the tether molecules enhance the membrane’s distance from the substrate (~17Å), thus enhancing our ability to incorporate large macromolecules into the membrane. We have successfully created lipid-conjugated polymer blends, where patterns of polymers can grow lipid domains into defined architectures.

Toward developing and assembling metal nanoclusters (DNA-AgNC) that enable control of electromagnetic fields or light-harvesting, we have created NanoCluster Beacons that turn on from dark to bright upon assembly with enhancer DNA sequences. Further, we have evolved DNA templating sequences so as to dramatically increase the photo- and shelf-stability of the resultant AgNC. For the first time in the literature, we have shown by Ag K-edge EXAFS that these materials are clusters with appropriate Ag-Ag bonds distances, Ag-DNA bonds, and cluster sizes dependent on DNA sequence. These EXAFS studies are consistent with SANS and SAXS analysis of the DNA templated cluster size. We can create chimeras of DNA that template the AgNCs and bind proteins or complimentary DNA. From these chimeras, we have created DNA-lipid adducts and have created assemblies of AgNC and carbon nanotubes with highly efficient energy transfer and CNT photophysics.

Active Assembly of Dynamic and Adaptable Materials

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Funding:	$1,290,000

PROGRAM SCOPE

The objective 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 can duplicate 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 tasks: (1) *Active Protein Assemblies*, which involves using kinesin and tubulin in artificial systems to manipulate hybrid and composite nanomaterials, and (2) *Artificial Microtubules*, which is focused on the design and development of robust artificial analogues to the energy-consuming protein tubulin. In the Active Protein Assembly task, work has focused on applying microtubule and kinesin dynamics to actively assemble non-equilibrium structures such as ring nanocomposite, lipid nanotube networks, and heterostructured nanowires. Work in the Artificial Microtubule task 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 2012 HIGHLIGHTS

Highlights in the Active Protein Assemblies task include the following:

- Ring nanocomposites – Kinesin transport has been used to dynamically assemble ring structures composed of microtubule filaments and semiconductor nanocrystals. We recently evaluated the ability to control nanocomposite morphology by varying the thermodynamic and energy-dissipative components, and using microfabricated substrates to induce confinement effects.

- Microtubule self-organization – Traditional models for microtubule growth suggest that polymerization occurs via the addition of tubulin. Recently, we experimentally demonstrated that stabilized microtubules can self-organize end-to-end and form high-aspect heterostructured nanowires without the addition of tubulin.

Highlights on the Artificial Microtubules task include the following:

- Theory/Modeling – We have applied molecular dynamics simulations to understand the basics of microtubule assembly. Simulations show that the shape of the monomeric building blocks, as well as the strength, distribution, and local symmetry of binding sites, play critical roles in the assembly of hollow, tubular structures.
- Peptide-based assemblies – We have designed and developed a wedge-shaped peptide system that is capable of self-assembling into nanofibers. Similar to the molecular dynamics simulations, this peptide system has enabled us to change the charge distribution and amphiphilicity in the building blocks, and study how these factors affect nanofiber assembly.

Molecular Nanocomposites

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Students:	3 Postdoctoral Fellow(s), 1 Graduate(s), 2 Undergraduate(s)
Funding:	$1,295,000

PROGRAM SCOPE

The Molecular Nanocomposites project explores the assembly and unique emergent properties of nanocomposite materials created using solution-based processing methods. The project develops fundamental understanding of the principles that govern the formation and function of novel nanocomposite materials. Scientific issues include (1) the synthesis of complex building blocks, (2) self- and directed assembly, (3) dynamic reconfigurable materials assemblies, (4) interfacial phenomena in organic-inorganic nanomaterials, and (5) properties of nano- to microscale materials assemblies (e.g., transport, electronic and optical behavior, interfacial chemistry, etc.). The project comprises two subtasks: (1) adaptive and reconfigurable nanocomposites, which explores the basic science associated with the use of energy consuming, switchable, and/or responsive components to create programmable and/or reconfigurable nanocomposites; and (2) complex nanocomposites, whose goal is the discovery and understanding of new chemical synthesis and assembly methodologies to construct and integrate complex porous and composite materials exhibiting structure and function on multiple length scales.

FY 2012 HIGHLIGHTS

Subtask 1 – Adaptive and Reconfigurable Nanocomposites group: This group (Huber, Sasaki, Stevens, Wheeler) is pursuing a coordinated modeling, synthesis, assembly, and reconfiguration approach to nanocomposites with controllable function.

(1) Programmable Molecules – New classes of surfactants have been developed with head groups whose interactions can be switched using a thermally activated phase transition, and a rudimentary phase diagram has been mapped.

(2) Programmable Assemblies – The thermally programmable surfactant has been inserted into lipid bilayers. Head group switching has been shown to reversibly program the size and shapes of vesicles and the switching of the architectures formed between gold nanorods.

(3) Magnetic Nanoparticles – New methods have been developed to synthesize low size dispersity iron and magnetite nanoparticles for magnetically programmable nanocomposites.

(4) Theory/Modeling – Models developed to probe the mechanisms of the thermally-activated transition in polymer head groups based on the competition between hydrogen bonding and entropy.

Subtask 2 – Complex Nanocomposites group: This group (Brinker, Fan, Kaehr) has advanced the field of molecular nanocomposites in several substantive directions:

(1) Cooperative Self-Assembly (CSA) – Used CSA for non-covalent assembly of mono disperse fluorescent organic/inorganic composite nanoparticles to tune full color spectrum. Non-covalent self-assembly between block copolymer and rare earth (RE) ions overcomes fluorescent quenching and leads to monodisperse, optically active organic/inorganic composite nano particles with tunable emission.

(2) Pressure-Directed Assembly (PDA) – Showed for the first time that application and release of a hydrostatic and/or uniaxial pressure field causes the unit cell of a 3D metallic nano particle array to shrink or expand, allowing precise tuning of interparticle symmetry and spacing, ideal for the controlled investigation of distance-dependent energy interactions and collective chemical and physical properties.

(3) Protocellular Architectures – Composed of fluid, dynamically reconfigurable phospholipid bilayers on self-assembled nanoporous silica particles, these platforms enable the compartmentalized chemistry and functions of living cells.

(5) Silica Cell Replication – Discovered/developed a new class of biocomposite materials based on external/internal silica replication of cells and multicellular organisms, with broad potential for biopreservation, catalyst stabilization, and synthesis of hierarchical materials.

(6) Biocompatible Microfabrication – Developed technique to isolate single cells in 3D hydrogel chambers using biocompatible multiphoton lithography (bio-MPL) that allows subsequent analysis and confinement of cell progeny. Extended 3D micro-nanolithographic methods to catalytic and responsive material systems providing a library of 3D direct write functioning materials that mimic cellular systems.

Molecularly Engineered Biomimetric Nanoassemblies

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Funding:	$70,000

PROGRAM SCOPE

The program aims to develop self-assembly and biologically-assisted assembly methods for the control of functional responses in complex, multi-component materials. The overall motivation is derived from an examination of natural systems that demonstrate exquisite manipulation and transduction of optical energy. We are interested in developing assemblies of nanomaterials that mimic two particular functions of natural systems: photo-induced charge separation and control of light-harvesting (or manipulation of electromagnetic fields). An important aspect of natural systems is their hierarchical organization, which allows for control and manipulation of energy across multiple length scales in a spatially directed manner. In many cases, this hierarchical organization is associated with complex membrane assemblies. Thus, we also explore the integration of functional synthetic nanomaterials with complex membrane-based architectures in order to generate materials with energy-relevant functions that demonstrate larger-scale organization similar to that found in natural systems. Functionally active synthetic materials under study include conjugated polymers and polyelectrolytes, carbon-based nanomaterials, and luminescent noble-metal nanoclusters. Approaches used include a combination of material synthesis and fabrication, static and time-resolved spectroscopies, optical and scanning probe microscopies, structural characterization, and modeling and analysis.

FY 2012 HIGHLIGHTS

Sandia has a small part of the overall project, which is led out of LANL. At Sandia, over the past year we have been studying the organization of molecular assemblies in supported lipid membranes and the interfacial interaction of conjugated polymers with those assemblies. Optimized membrane compositions and solution conditions enabled us to prepare domains enriched in negative charge providing site selective adsorption of positively charged conjugated polymers. Further, through a CINT project we are developing patterned lipid-tethered surfaces using e-beam lithography to induce the directed formation of membrane domains. Our future research will concentrate on combining these two efforts to generate patterned assemblies of conjugated polymers and fullerenes.

Recently, we successfully demonstrated the directed formation of lipid domain architectures to enable the selective adsorption and surface patterning of conjugated polyelectrolytes. Domain structures in supported lipid bilayers were patterned by a surface scribing technique on the substrate, hence creating a pattern of nucleation sites for growing gel phase domains. We are currently exploring the physical and chemical characteristics of the scribed substrate that promote domain nucleation.

Clathrin Biotemplating

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Funding:	$491,000

PROGRAM SCOPE

The focus of this program is to identify self-assembly mechanisms and building-block properties for deterministic formation of complex three-dimensional organic/inorganic constructs. By appropriate selection of architecture, materials, and morphology, these materials will lead to fundamentally new designs for bio-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 the dynamic assembly of complex biopolymer architectures. While previous studies of biotemplates have focused on the biochemical aspects of assembly at physiological conditions, our team is focused on the wide diversity of assemblies that can be made under varying conditions by applying insight into fundamental physical mechanisms. Our integrated approach offers a new range of perspectives to address biopolymer assembly. Our recent collaborative effort has focused on experimental and theoretical phase diagram predictions for the self-assembly of clathrin protein and the non-covalent, site-specific functionalization of these protein assemblies to template the synthesis of inorganic nanoparticles.

FY 2012 HIGHLIGHTS

We studied the unique self-assembly capabilities of clathrin, a trimeric protein that assembles into a range of 2D and 3D mesoscale structures. Through the concerted use of dynamic light scattering, cryo transmission electron microscopy, and theoretical modeling, we discovered that 3D disordered clathrin aggregates undergo large scale structural rearrangements resulting in the self-assembly of discrete, spherical cage structures. We then demonstrated a novel strategy to functionalize these 3D protein assemblies by mimicking the evolved biological versatility of clathrin to perform multiple functions. Through site-specific, non-covalent interactions with designed peptides, the clathrin cages were used as templates for the synthesis of gold, cobalt oxide, and titania nanoparticles. Current efforts aim at the simultaneous nucleation of multiple inorganic species at distinct epitope sites on the clathrin structure.

Electron and Scanning Probe Microscopies

Institutions Receiving Grants

Development and Application of In Situ Nanocharacterization to Photocatalytic Materials for Solar Fuel Generation

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Funding:	$145,000

PROGRAM SCOPE

Photocatalysis has the potential to play an important role in the development of sustainable energy technologies. In principle, hydrogen can be generated from water and carbonaceous fuels can be generated from CO_2 using photocatalytic or electrophotocatalytic processes. An advantage of this approach to solar energy is that the energy of the sun is simultaneously captured and stored in a fuel molecule. The current efficiency and long-term performance of photocatalysts for solar fuel generation is very low, and there are many fundamental problems that must be solved related to photon absorption, charge separation, and catalytic activity. The scope of this project is to develop novel in situ electron microscopy techniques for probing structure-reactivity relations in photocatalytic materials. Specifically, we are developing a variable wavelength light illumination system which will allow photocatalysts to be studied with atomic resolution under near reactor conditions. This instrumentation has now been developed, and we are currently investigating the surface changes taking place on bare and functionalized titania nanoparticles during photon illumination in atmospheres of water, hydrogen, and vacuum. The fundamental information that emerges from this project should lead to a deeper understanding of the effect of light, heat, and gas on the properties of nanomaterials relevant to solar fuels.

FY 2012 HIGHLIGHTS

A system for illuminating a sample in situ with visible and ultraviolet light inside an environmental transmission electron microscope was designed and constructed. The system includes a high brightness broadband light source with optical filters, a fiber to guide the light to the sample, and a mechanism for precisely aligning the fiber tip. The system has been installed and tested and can deliver light over the range 200-800 nm onto an electron microscope sample with an intensity in excess of 10 suns. This system has been employed to perform an atomic-level investigation of the surface structure of anatase nanocrystals under conditions relevant to gas phase photocatalytic splitting of water. When the titania is exposed to light and water vapor, the initially crystalline surface converts to an amorphous phase one to two monolayers thick. Spectroscopic analyses show that the amorphous layer contains titanium in a +3 oxidation state. The amorphous layer is stable and does not increase in thickness with time and is heavily hydroxylated. This disorder layer will be present on the anatase surface under reaction conditions relevant to photocatalytic splitting of water.

Nanoscale Imaging of Electrostatic and Magnetic Fields

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Funding:	$140,000

PROGRAM SCOPE

The overall research objectives of this program are to observe and to quantify nanoscale electrostatic and magnetic fields using the technique of off-axis electron holography. This powerful electron-microscopy-based technique enables imaging and quantification of electromagnetic fields based on precise measurement of the phase changes of the electron wave that has passed through the sample. Both electrostatic and magnetic fields can be measured with high precision and nanoscale resolution. In this project, targeted semiconducting materials and devices as well as topical magnetic materials, especially nanostructures, are being investigated. One major focus of this research program emphasizes the electrostatic potential profiles that are developed across undoped and doped semiconductor heterojunctions. The influence of strain, dopant distributions, and in situ biasing on band offsets and charge accumulation in Group-IV nanowire heterostructures and devices will be assessed. In addition, attention is being directed towards the potential profiles present across III-V/II-VI heterojunctions, which are of considerable interest for ultrahigh-efficiency multi-junction solar cells. The second focus of this research relates to magnetic materials of much contemporary interest for compact memory and logic device applications. The generation of magnetic domains and the propagation of domain walls (DWs) in ferromagnetic nanowires will be studied, with particular attention being given to comparing magnetic-field-driven and current-induced DW motion and the competing effects of thermal annealing.

FY 2012 HIGHLIGHTS

Two papers published in FY 2012 (Applied Physics Letters, 99, 10, 1328-1332; Advanced Materials, 24, 10 1328-1332) highlight some of our work using electron holography to measure nanoscale electrostatic fields. Other studies on electrostatic fields have involved investigations of junctions in nanowires of Si and SiGe. Our investigations of nanoscale magnetic systems have included GaAs/Fe core-shell nanowires. Initial results suggest remanent states that are not well-understood. We have also been investigating the magnetic behavior of chains or varying length of Co/CoO nanoparticles.

Quantitative Electron Nanodiffraction

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

PROGRAM SCOPE

By developing the methods of quantitative electron nanodiffraction in an field-emission electron microscope, we aim to determine the atomic structure and mechanisms for a range of energy-related materials, including electronic oxides, battery materials, and semiconductors.

FY 2012 HIGHLIGHTS

(1) We have devised a new method of direct-write subnanometer electron-beam lithography [Appl Phys Letts. In press. (2012)]. With this, we have written grating structures of nanometer period, and obtained electron diffraction patterns from them.

(2) We have determined the nature of the two-dimensional phase transition which occurs at interfaces in artificial oxide multilayer materials at low temperature. These structures have new controllable electronic properties (Phys Stat Sol A 209, 1322).

(3) We have observed and analyzed a dose-rate threshold in beam-damage for electron microscopy, not seen before [Ultramic. 113, 77 (2012)].

(4) We have determined the ordering of Ca ions in a silicate glass, using electron-loss near-edge structure [Appl. Phys. 110, 013518, (2011)]. These glasses have important applications in photonics, waste storage, and communications.

Structural Studies of Amorphous Materials by Fluctuation Electron Microscopy

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Funding:	$215,000

PROGRAM SCOPE

Fluctuation electron microscopy (FEM) examines the statistics of electron diffraction from small regions of a thin sample. Consequently, the variability of diffraction between regions is revealed. These diffraction variations, which are essentially speckle, tell us a lot about any subtle medium-range ordering that may exist in the sample. This variability is not probed by conventional high-resolution diffraction that examines a sample average only.

The project scope is to develop the analytical tools that make FEM more quantitative. To do this, methods for inverting four-body diffraction data will be developed. Further, the FEM method will be applied to the investigation of amorphous materials that are being developed for energy applications.

FY 2012 HIGHLIGHTS

There has been longstanding debate about the nature of amorphous silicon. Our results, using an experimentally constrained structural relaxation (ECSR) procedure, show that amorphous silicon, even when thermally relaxed, is not a true continuous random network (CRN). Instead, it is better modeled as a paracrystalline structure that contains small regions, about 1 – 2 nm in extent, that are topologically cubic. This means that in some regions, the structure contains particulates of crystalline silicon that are defective or are experiencing strain gradients. This result was published [Science 335, 950 (2012)] and has attracted a Comment that defends the CRN model, and our Response that defends our results, that will appear in print in *Science* soon.

We have applied the FEM method to the nitrogen-doped amorphous diamond films that are being developed as devices that convert heat and solar energy to electrical energy. We are exploring the relationship between device efficiency and structural disorder, as well as developing the FEM method on our new aberration-corrected electron microscopes.

STM Studies of Spin-Orbit Coupled Phases in Real- and Momentum-Space

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Funding:	$154,000

PROGRAM SCOPE

The recently discovered class of spin-orbit coupled materials with interesting topological character are fascinating both from fundamental as well as application points of view. The non-trivial topological properties of topological insulators 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. The goal of this project is to use low temperature scanning tunneling microscopy (STM) to study materials with topological phases in both real- and momentum-space. The materials we propose to study include 3D topological insulators and Skyrmion systems. Using low temperature scanning tunneling spectroscopy and related techniques, our objectives answer fundamental questions such as the following. *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 and how does the position of the Fermi energy with respect to the bulk bands influence the ground state and low energy excitations? How do we realize 2D topological insulators in mono- or bi-layer thin films? Can we see the edge modes in 2D topological insulators? What are their electronic signatures?*

FY 2012 HIGHLIGHTS

The grant start date was August 1, 2012. In the first two months, we identified the evaporators that we will be using to make topological insulator thin films and began STM studies of ex-situ grown thin films made by our collaborators.

Materials Properties at Interfaces in Nanostructured Materials: Fundamental Atomic Scale Issues

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Funding:	$160,000

PROGRAM SCOPE

The aim is to develop a robust method to quantify the atomic scale changes in structure, composition, and bonding that occur at grain boundaries. To truly quantify the properties of grain boundaries, any atomic scale study must give statistical relevance to the analysis. For example, *how many grain boundaries, dislocation cores, or point defects were analyzed to produce the quoted result? How were the grain boundaries produced and what beam conditions were used to make sure the boundary was stable during the analysis?* In addition to an increase in spatial resolution, the advent of aberration correctors has provided a stability and robustness of experimental approach that means the experiment can be precisely defined and the statistical variations across many images can be correlated and quantified. This research will use these features of aberration correction to build on the statistical crystallography methods developed for structural biology and applied previously in materials science to study doping changes in bulk materials. By applying these methods to grain boundaries (i.e., extended defects where the symmetry changes), this work significantly expands on the previous applications. Experiments will also feature a set of unique in-situ stages that will allow the chemistry of the grain boundaries to be modified inside of the microscope. Research will focus on grain boundaries in $SrTiO_3$ and CeO_2 to act as prototype systems for superconductors, ferroelectrics, and ionic conductors. Through such a detailed systematic analysis of grain boundaries, the most important compositional and structural effects controlling properties can be ascertained, and the mechanism by which grain boundary properties can be manipulated on the atomic scale will be determined.

FY 2012 HIGHLIGHTS

We have shown that statistical analysis of images acquired from a large area of grain boundary is an effective route to understanding the variation in boundary structure that occurs to accommodate non-stoichiometry. In the case of the $SrTiO_3$ 22.6° ∑13 (510)/ [100] GB, the symmetric structures observed from a micron-long GB can be categorized as two different competing structural arrangements. First-principles density functional theory has been used to quantify the role that non-stoichiometry plays in determining the energies of these boundaries. In addition, a general model for the structure of grain boundaries in dense packing materials systems (fcc metal, perovskite, fluorite, etc.) has been developed based only on the crystallography of the parent structures. Changes away from the predicted grain boundaries can be interpreted as showing the frustration of symmetry caused by point defects. This general model for grain boundary structures can, in principle, provide a means to infer the structure-property relationships in broad classes of materials.

Beneath and Between: Structural, Functional, and Spectroscopic Measurements of Buried Interfaces and Interactions

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Funding:	$200,000

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 will develop the ability to measure the orientation of buried functionality.

FY 2012 HIGHLIGHTS

We appear to have made the first observation of a 2D plastic lattice. We used low-temperature STM and barrier-height imaging in a carboranethiol monolayer to measure the aligned dipoles of the molecules offset from the topographic maxima of the features due to the molecules in conventionally recorded STM images. We are developing algorithms to make these determinations automatically.

We have made significant headway in identifying the positions and orientations of other molecules, such as self-assembled peptides. Further measurements seek to identify and to locate multiple bonds, heteroatoms, molecule-substrate contacts, and molecule-molecule contacts.

In Situ Analytical Electron Microscopy for Understanding Structure Evolution and Composition Change in High Energy Density Electrode Materials in Lithium Ion Batteries

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Funding:	$180,000

PROGRAM SCOPE

The objectives of this proposed work are to develop new innovative experiment techniques for understanding the chemistry and structure of the bulk and interfaces of electrochemical active materials and, more importantly, how they change with electrochemical processes in situ. Most of the Focused

Ion Beam (FIB) fabrication of nanobattery will be carried out locally in San Diego through FIB access at Qualcomm Inc. and the Calit2 FIB facility at UC Irvin. Pulsed laser deposition fabrication of all solid state thin film batteries has been established, and a new design of optimum solid state batteries is achieved in collaboration with Dr. Nancy Dudney at Oak Ridge National Laboratory. The STEM/EELS work is carried out both locally at UCSD as well as at the Center for Functional Nanomaterials (CFN) at the Brookhaven National Laboratory through the user proposal and close collaboration with Dr. Feng Wang. With the combination of the expertise, instrumentation and protocol developed, in situ TEM observation of electrochemical phenomena in a thin film nano-battery, prepared from a functional nanobattery specimen, will be used to gain a fundamental understanding of structural evolution and composition change in electrode and electrolyte materials in lithium ion batteries.

FY 2012 HIGHLIGHTS

Several major steps toward the in-situ TEM observation of electrochemical dynamics have been successfully completed thus far. We have successfully fabricated all solid-state batteries by PLD, and in situ biasing in the SEM and TEM with pA current control has been achieved. We optimized the nano-battery TEM specimen preparation and 3D visualization, with minimization of electron beam and ion beam damage. We demonstrated for the first time that FIB-processed solid state batteries can retain their full electrochemical functionality. The work has been presented in 2012 European Microscopy Society as an invited talk, and several manuscripts have been submitted for peer-reviewed journals.

Phonons and Electrons in Thin Complex Oxides

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Funding:	$180,000

PROGRAM SCOPE

The objective of the program is to develop new approaches to understand and control phase transformations in complex oxide thin films as their dimensions approach the nanoscale. New methods are developed to grow perovskite titanates with high structural perfection, high purity, and low intrinsic defect concentrations by oxide molecular beam epitaxy. The project also builds on the unique capabilities of scanning transmission electron microscopy techniques, in particular, quantitative high-angle annular dark-field imaging. The combination of macroscopic and microscopic techniques provides a wealth of information about transport, vibrational modes, and defects in ultrathin oxide films.

FY 2012 HIGHLIGHTS

We showed that a novel, quantitative, scanning transmission electron microscopy (STEM)-based diffraction technique developed by us, *position-averaged convergent beam electron diffraction (PACBED)*, allows for quantifying oxygen octahedral rotations in perovskites with unit-cell spatial resolution. We demonstrated the capabilities of the PACBED method by quantifying the NiO_6-octahedral tilts in ultrathin $LaNiO_3$ films as a function of film strain. We showed that PACBED allows for the investigation of the local structural origins that determine the properties of nanoscale heterostructures with distorted perovskites, including strongly correlated materials, such as the rare earth nickelates or titanates.

Hydrogen Generation using Integrated Photovoltaic and Photoelectrochemical Cells

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Funding:	\$0.00 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

The objective of this proposal is to design, fabricate, and characterize interfaces in nanocomposite materials of interest for a variety of applications including energy conversion. The emphasis is to probe and understand the detailed structural properties and associated charge carrier dynamics using a combination of techniques. Multiple component nanocomposite materials can exhibit unique and improved optoelectronic properties when properly designed and fabricated. Specifically, we will focus on novel nanocomposite structures: a core/spacer/shell nanostructure with a large bandgap metal oxide (MO) semiconductor for the core, an insulator as a spacer, and a small bandgap semiconductor as the shell. The small bandgap semiconductor, e.g., quantum dots (QDs) with tunable light absorption, acts as the light absorber and injects electrons into the large bandgap MO. The electrons injected into the MO can be used for driving photoreduction reactions, e.g., hydrogen generation from protons, while the hole left in the QDs can drive photooxidation. The insulator spacer is used to modulate and control the interaction and charge injection between the MO and QDs. The spacer can be in the form of a solid insulator such as SiO_2 or small organic linker molecules that are used to tune the interaction between the sensitizer and MO.

For the investigation, we will first design and fabricate the nanocomposite structures, and then carry out a systematic investigation of their structural, optical, dynamic, and photoelectrochemical (PEC) properties with focus on the interfacial region since it is the interface that determines the characteristics as well as functionalities of such nanocomposite materials. In addition, we will explore their application in a prototypical PEC device designed for hydrogen generation from water splitting. We anticipate that the nanocomposite structures will show improved PEC performance. In addition, this project will provide better fundamental understanding of the relation between characteristics of nanocomposite structures and interfaces between their constituting components.

FY 2012 HIGHLIGHTS

We have successfully fabricated metal oxide nanostructures and synthesized semiconductor quantum dots with improved optical properties. We have investigated their interfacial charge injection dynamics using ultrafast laser techniques and evaluated their PEC performance. One important discovery is that chemical treatment of the metal oxide significantly improves charge transport. In the next period, we envision combining QD sensitization with chemical modification to achieve synergistic effects in enhancing the overall PEC performance. We also plan to more systematically vary and control the surface properties of the QDs and MOs that are expected to be important for PEC properties.

Materials Applications of Aberration – Corrected Lorentz Microscopy

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Funding:	$150,000

PROGRAM SCOPE

In this project, we build upon our earlier work in vector field electron tomography, and we aim to create an automated iterative approach to extract simultaneously the magnetic and electrostatic potentials from tomographic data sets with a target magnetic resolution of just a few nanometers, an order of magnitude better than the best reconstructions thus far. In addition, we build on theoretical/modeling advances to study, both experimentally and through modeling, the behavior of magnetically frustrated 2D systems fabricated by electron beam lithography of permalloy thin films. These systems are patterned in a variety of lattice configurations at a length scale that allows the individual elements to be in a single domain state. Aberration-corrected LTEM is a necessary tool to elucidate the local magnetization state(s), in particular the presence of magnetic monopoles (local violations of the spin-ice rule) and Dirac strings. Underlying all of the experimental observations, we study the concept of "magnetic resolution"; and we attempt to find a precise answer to the questions of how one defines resolution in LTEM and determines its resolution limits. The project will have several important outcomes/impacts: an efficient, accurate, iterative tomographic reconstruction technique, including an experimental protocol, which can be used in contemporary aberration-corrected microscopes to obtain simultaneously the 3D magnetic vector potential and the scalar electrostatic potential; a clear understanding of the concept of "magnetic resolution" in aberration-corrected LTEM; and a sound experimental and modeling methodology for the study of magnetic frustration in 2D spin-ice lattices based on both uniform and k-uniform lattices. We anticipate that the results from the proposed research will lead to novel insights into 3D magnetism and the behavior of magnetically frustrated 2D systems, as well as to a better understanding of aberration-corrected Lorentz TEM.

FY 2012 HIGHLIGHTS

We have created a novel numerical approach for the simulation of the magnetic phase shift of an object with arbitrary shape and arbitrary magnetization configuration. This approach can be used in iterative tomographic reconstruction algorithms, since it allows for the efficient computation of magnetic phase shift when a single object voxel is modified. We have also created a new version of the Transport-of-Intensity equation, which allows us to separate the electrostatic and magnetic contributions before we reconstruct the phase shifts.

Mapping Interactions in Hybrid Systems with Active Scanning Probes

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Funding:	$150,000

PROGRAM SCOPE

The goal of this research will be 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 2012 HIGHLIGHTS

Since the beginning of this project in the summer of 2012, we have completed design and construction of the scanning probe microscope system and are in the process of evaluating and optimizing the performance using commercial probes. Meanwhile, fabrication of custom probes is underway. We are characterizing the properties of magnetic microstructures and individual semiconductor nanocrystal quantum dots separately. These components will then form the basis for a hybrid system, which we will study in our scanning probe system. In the next period, we will bring these components together and perform initial measurements using our scanned active probes.

Grain Boundary Complexions and Transitions in Doped Silicon

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

PROGRAM SCOPE

The goal of this project is to advance the fundamental knowledge of grain boundary (GB) complexions (i.e., two-dimensional interfacial phases) and associated GB "phase" transitions. In the past four years, significant progress has been made in several grounds. First, a bilayer interfacial phase, which had been directly observed by microscopy only in complex ceramic systems in prior studies, has been identified in simpler systems such as Au-doped Si and Bi-doped Ni in this study, where the interpretations of the their formation mechanisms and microscopic images are less equivocal. Second, convincing evidence for the existence of a first-order GB transition from a nominally "clean" GB to a bilayer adsorption interfacial phase has been revealed for Au-doped Si; the confirmation of the first-order nature of interfacial transitions at GBs, which was rare in prior studies, is scientifically significant and technologically important. Third, the bilayer interfacial phase discovered in Bi-doped Ni has been found to be the cause of the mysterious liquid metal embrittlement phenomenon in this system; the exact atomic level mechanism of this phenomenon has puzzled the materials and physics communities for over a century. Finally, significant advancements have been made to establish phenomenological thermodynamic models for GB complexions and transitions.

FY 2012 HIGHLIGHTS

This research project was successfully completed by July 2012. Highlights of FY 2012 include confirming and analyzing the first-order nature of interfacial complexion (phase) transitions. Since GB complexions and (phase) transitions can often control the transport, mechanical, and physical properties of a broad range of metallic and ceramic materials, the fundamental knowledge generated by this project can have broad impacts on materials design. In this regard, understanding and controlling GB phase behaviors (complexions and transitions) can be an important component for the "Materials Genome" project.

Nano-Imaging and –Spectroscopy of Correlated Electron Materials

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Funding:	$190,000

PROGRAM SCOPE

We perform nano-optical imaging and spectroscopy of the nano-domain phase behavior and order phenomena in correlated electron materials. This work is based on our development of variable temperature scattering scanning near-field microscopy (*s*-SNOM) in combination with linear, nonlinear, and ultrafast spectroscopy, providing spectroscopic specificity in terms of electronic and vibrational resonances, structural symmetry, and ultrafast dynamics with simultaneous nanometer spatial resolution.

Of the different correlated electron materials, transition metal oxides are often characterized by competing nearly degenerate states of coupled charge, orbital, spin, and lattice degrees of freedom. In our project, we focus specifically on the study of materials that exhibit one or a combination of the following properties: colossal magneto-resistance (CMR), metal-insulator transitions (MIT), and multi-ferroicity. Frustration and degenerate ground states lead to phase competition and coexistence of multiple phases with structural and electronic inhomogeneities and mesoscopic spatial phase separation over 5 orders of length scale. Understanding this complex phase behavior is important from both a fundamental and a technological perspective. First, the domain texture and topology are thought to arise from and reflect the microscopic interactions in these systems. Second, the domain architecture affects macroscopic properties, including transport (percolation) or magneto-electric coupling and poling in multiferroics. Our unique ability to resolve the nano-phase behavior of different order parameters, and to probe its dependence on internal and external parameters, would bring us closer to understand the underlying microscopic processes, and with that the means to control the macroscopic material properties.

FY 2012 HIGHLIGHTS

We have developed the first versatile and multi-modal scattering-type scanning near-field optical microscope (*s*-SNOM) operating under cryogenic and variable temperature (∼ 20 - 500 K) and compatible with high magnetic fields (up to 18 T). The instrument features independent tip and sample scanning (scan range 50 µm × 50 µm × 24 µm) and free-space light delivery with an integrated off-axis parabolic mirror for tip-illumination and signal collection with a numerical aperture of N.A.=0.45. The optics operate from the UV to THz range allowing for continuous wave, broadband, and ultrafast *s*-SNOM spectroscopy. We have demonstrated its performance with mid-infrared Drude response *s*-SNOM probing of the domain formation associated with the metal- insulator transitions of VO_2 ($T_{MIT} \simeq 340$ K) and V_2O_3 ($T_{MIT} \simeq 150$ K). This instrument, with 10 nm spatial resolution, enables the study of mesoscopic order and domains of competing quantum phases in correlated electron materials over a wide range of controlled electric and magnetic fields, strain, current, and temperature.

Switching in Solid State Memories via Nucleation and Growth Mechanisms: Causes and Effects at the Nanometer and Nanosecond Scale

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Funding:	$140,000

PROGRAM SCOPE

Operating speeds, reliability, and energy consumption in various data storage systems correlate with the mechanisms of switching between discrete data states. But these dynamic processes are exceedingly difficult to directly interrogate because they occur in nanoseconds and at the nanometer length scale. This project therefore develops and applies novel variations of high speed scanning probe microscopy capable of manipulating and mapping data states under such conditions, in fact providing nanoscale movies of the entire process. Uniquely, this permits direct observation of (1) the onset of switching, by mapping nucleation site positions and densities as a function of energy; (2) the evolution of a switched area by growth, including mapping any direction dependencies; and (3) the interplay between these distinct mechanisms and their relationship to composition, fabrication, or even cycling over many orders of magnitude of switches. This provides insight into new methods to engineer future devices with improved performance and energy efficiency.

FY 2012 HIGHLIGHTS

As intended, the project has recently focused on switching dynamics in several distinct data storage systems. In the first case, ferroelectric thin films (PZT) have been electrically switched with narrow but high amplitude pulses engineered to enhance initial nucleation site densities, followed by more energy-efficient, low-voltage biasing which grows the seeded sites to complete the switching process. In more complex multiferroic films (BFO), for the first time, discrete steps in a continuous switching process have been resolved. This revealed not just the switching process but also the unexpected occurrence of backswitching events which diminish both a device’s energy efficiency as well as its long-term reliability. Finally, in chalcogenide-glass based memory systems, switching has been achieved upon pulses as narrow as 10 nsec, for the first time, with a SPM. This has enabled the energetic and spatial uniformity of switching to be uniquely investigated in this distinctly different but also promising class of data storage materials.

Using Interfaces to Create Strongly-Coupled Magnetic Ferroelectrics via Atomic-Scale Heteroepitaxy

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Funding:	$340,000

PROGRAM SCOPE

In this program, we are developing the scientific ideas necessary to apply a materials design paradigm to the creation of multiferroics with unprecedented coupling between ferroelectric and magnetic order parameters, i.e., strongly-coupled magnetic-ferroelectrics. This project has two research objectives. The first 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, but we recently predicted a class of materials that we call hybrid improper ferroelectrics where octahedral rotations are exploited to enable such switching. 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. Our second objective is to create magnetic ferroelectrics where the magnetism can be turned on by applying an electric field. Such an effect has also never been demonstrated, but we predicted it to occur in appropriately strained $EuTiO_3$. Our subsequent observation of a strain-induced ferromagnetic ferroelectric state in strained $EuTiO_3$ confirms the microscopic coupling model and calculations underlying this prediction. The simultaneously ferromagnetic and ferroelectric state that we induced in $EuTiO_3$ with strain created the world's strongest ferromagnetic ferroelectric, in agreement with our first-principles prediction. This verification strongly motivates our desire to turn on the strong ferromagnetism in appropriately strained $EuTiO_3$ by the application of a modest electric field. By creating new interface phases and atomically thin layers, we are achieving, through rational design, materials systems that provide the structural and magnetic properties—which are often mutually incompatible in bulk systems—needed to realize such a strongly coupled magnetic-ferroelectric.

FY 2012 HIGHLIGHTS

Using first principles calculations, we showed that the strong coupling between the rotations of oxygen coordination octahedra in complex oxides (a type of lattice distortion that is ubiquitous in complex electronic materials) and magnetic properties represents an opportunity to understand and create new multiferroics. We established general design rules and identified new classes of materials (i.e., known Ruddlesden-Popper phases as well as artificial superlattices) that should exhibit such behavior. Our work showed, for the first time, how octahedral rotations simultaneously induce and thereby naturally couple ferroelectricity, magnetoelectricity, and ferromagnetism—a breakthrough in the field of multiferroics. The new octahedral-rotation-based mechanism enables an applied electric field to globally and deterministically switch the magnetization by 180° in a single-phase multiferroic material.

Following our materials-by-design approach, we have grown epitaxial thin films of the materials identified by reactive molecular-beam epitaxy and are characterizing their structure and properties. One of the experimental issues that we have run up against is the difficulty in switching the materials we have made to date through the application of an electric field. This difficulty has motivated our theory effort to identify materials within this new class of multiferroics having lower activation barriers to switching.

Transport and Imaging of Mesoscopic Phenomena in Single and Few Layer Graphene

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Funding:	$400,000

PROGRAM SCOPE

The research objective of this project is to investigate novel quantum phenomena in single and few layer graphene [FLG]. 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 will 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 and superconducting gates, and contacting graphene with novel materials. Our focus will be on extremely high quality FLG fabricated either by suspending above a substrate or using hBN 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 (S-G) devices.

FY 2012 HIGHLIGHTS

In our recent experiments in single, bi- and twisted bilayer graphene, we have focused on transport and imaging spectroscopy in the quantum Hall regime, where novel collective many body phenomena stemming from interaction effects are most pronounced.

Our research efforts for the next years will focus on (1) transport and imaging of ultra-high mobility in single and few layer graphene, (2) induced superconductivity in single layer and few layer graphene, (3) proximity effect between superconductivity and quantum Hall physics, (4) transport and imaging of graphene in inhomogeneous magnetic fields, and (5) engineering topological phases in graphene by tuning electron-electron interactions. Such phases include quantum spin Hall and non-Abelian fractional quantum Hall states.

Electron Nanocrystallography of Complex Materials and Processes

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PROGRAM SCOPE

The goals of the proposed research are to develop quantitative and robust electron diffraction techniques for atomic structure determination of nanostructures and study their structural dynamics. The expected outcomes from the proposed research include determination of 3D structure of selected nanoparticles and determination of the symmetry and strain in nanometer-sized ferroelectric domains in relaxor ferroelectrics. The study of nanoparticles will be focused on understanding the role of defects in nanoparticle formation and how defects influence the surface structure of nanoparticles. The work is expected to extend our knowledge of the surface structure nanocrystals without defects, which was developed under the prior DOE support. The study in relaxor ferroelectrics is a new area for electron nanodiffraction. The ability to correlate the symmetry and strain using diffraction information is expected to improve our understanding of the structure of nanodomains and its impact on high electro-mechanical activity in relaxor ferroelectrics. The knowledge will enable discovery and control of optimal domain structure for electrical and mechanical coupling and sensing.

FY 2012 HIGHLIGHTS

In a paper published in *Ultramicroscopy*, we proposed a new algorithm to quantify symmetry recorded in convergent beam electron diffraction (CBED) patterns and to use it for symmetry mapping in materials applications. We evaluated the effectiveness of the profile *R*-factor (R_p) and the normalized cross-correlation coefficient (γ) for quantifying the amount of symmetry in a CBED pattern. Using the mirror symmetry as an example, we demonstrated that the normalized cross-correlation coefficient provides an effective and robust measurement of the symmetry recorded in experimental CBED patterns.

Using the above symmetry quantification method, we examined the symmetry of (1-x)Pb($Mg_{1/3}Nb_{2/3}$)O_3-x$PbTiO_3$ (PMN-xPT) single crystals in the morphotropic phase boundary (MPB) region at composition x=0. 31 (PMN-31% PT). On the macroscopic scale, x-ray diffraction (XRD) shows a mixture of strong and weak diffraction peaks of different widths. The closest match to XRD peak data is made with monoclinic Pm (M_C) symmetry. On the local scale of a few nanometers, CBED studies, with a 1.6 nm electron probe, reveal no obvious symmetry. A monoclinic Cm (M_A or M_B)-like symmetry could be obtained from certain regions of the crystal by using a larger electron probe size of several tens of nm in diameter. Thus, the macroscopic symmetry observed by XRD is a result of averaging from the local structure in PMN-31%PT single crystal. The lack of local symmetry at a few nm scale suggests that the polarization switching results from a change in local dipoles, which are not restricted to specific symmetry planes or directions.

Four-Dimensional Characterization of Dislocation-Defect Interactions in Aggressive Environments - A New Approach

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PROGRAM SCOPE

The goal of this project is to transform conventional electron microscopy from being a static two-dimensional technique to being a dynamic three-dimensional tool. We have shown that the constraints of forming a high-resolution electron tomogram can be relaxed by using knowledge of diffraction contrast imaging theory and dislocation characteristics as well as using a low resolution tomogram as the template for constructing a three-dimensional model. The challenge is to advance this technique further such that it can be combined with dynamic experiments in the transmission electron microscope. With this capability, it will be possible to periodically interrupt the dynamic experiments and acquire three-dimensional snapshots of the evolved state. This capability will be employed to explore how microstructure evolves during loading as a function of temperature, with particular attention being paid to how strain is transferred across interfaces in different crystal structures. The long-term impact of this work is it will provide the capability of four-dimensional characterization of how a system responds to an applied stimulus. The insights gained as to the evolutionary processes will inform simulation and modeling efforts that are aimed at advancing the state-of-the-art capabilities of predicting the response of systems exposed to stress and temperature.

FY 2012 HIGHLIGHTS

We have found that with surface markers, introduced either manually or via nano-scale surface particles, it is possible to reduce the requirements, angular range, number of images, and image quality and still attain a tomogram of sufficient quality to serve as a template for forming a three-dimensional model. This advance makes it feasible to combine this analysis method with dynamic in situ experiments. Using this combination, we have determined that in FCC metals, the magnitude of the increase in the strain energy density in the grain boundary due to strain transfer and that the local stress is an important but not controlling mechanism. This conclusion appears to be insensitive to the test temperature up to 673 K. In the next period, we will determine if the same driving force controls the transmission of strain in BCC metals as a function of temperature.

In-Situ TEM Observations of Degradation Mechanisms in Next-Generation High Energy Density Lithium-Ion Battery Systems

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Funding:	$150,000

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 2012 HIGHLIGHTS

We have demonstrated in-situ cycling of lithium ion batteries in commercial electrolytes within the TEM and have specifically characterized the mechanism for strain accommodation in Sn electrodes during lithiation and delithiation. The measurements reveal the formation of nanoporosity during the first delithiation cycle and partial degradation of the crystal structure (amorphization) and morphology during subsequent cycles. Our efforts have also focused on quantifying the role of the electron beam in affecting the response of model aqueous and non-aqueous liquid containing systems including $SiCl_4$, Ag-Ag_2SO_4 (aq.), and $Zn(NO_3)_2$- hexamethylenetetramine (aq.).

In Situ Characterization and Modeling of Formation Reactions under Extreme Heating Rates in Nanostructured Mutilayer Foils

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Funding: $0.00 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

Processing under extreme environments presents unique challenges and opportunities for controlling the microstructure and, thus, properties of materials. This research program uses advanced techniques for in situ structural characterization tightly coupled with a multiscale modeling effort to explore the effects of heating rate and composition gradients on interdiffusion and phase formation in nanoscale systems. Nanotructured multilayer foils provide ideal model materials for studying these effects in geometries and length scales that are amenable to both in situ characterization and continuum and atomistic modeling of the reaction process.

The experimental portion of our program emphasizes state-of-the-art in situ structural characterization techniques that enable us to study interdiffusion and phase transformations under rapid heating. In particular, we propose to exploit self-propagating exothermic reactions in multilayers to achieve heating rates of up to 10^8 Ks^{-1}, in addition to homogeneous thermal combustion reactions at more moderate rates (up to 10^5 Ks^{-1}). These conditions place stringent demands on the experimental techniques. We propose to use a combination of time-resolved x-ray microdiffraction, in situ x-ray reflectivity, and dynamic transmission electron microscopy (DTEM) to achieve the necessary spatial and temporal resolution to follow the transformation sequences in detail. These will be supplemented with ultrafast pyrometry, nanocalorimetry, and reaction front velocity measurements, all of which can be directly correlated with the structural observations.

The modeling effort has two primary goals. The first is to bridge the gap between experiments and atomistic simulations by using continuum models of self-propagating reactions as an intermediary. Atomistic simulations (Monte Carlo and molecular dynamics) will be used to generate thermodynamic and kinetic parameters as inputs to the continuum models, which will in turn allow predictions (of reaction velocity, for instance) that can be directly compared with experimental results. The second goal is to obtain direct insight into the atomic-scale processes associated with phase transformations under conditions of extreme heating rates and steep composition gradients. This will be done by using hyperdynamics (an accelerated molecular dynamics method) to simulate the evolution of the multilayer interfaces during the initial stages of the transformation.

Scientific issues of particular interest are diffusional asymmetries between the elements, nucleation and growth of transient phases, melting of either the elemental constituents or reaction products, and solid-state amorphization. Although the effect of rapid heating and steep composition gradients on these phenomena are relevant to many systems of technological interest, highly exothermic reactions in multilayers happen to provide a convenient and experimentally tractable setting for exploring them.

Size-Selected Clusters on Surfaces

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Funding:	$160,000

PROGRAM SCOPE

Clusters possess many novel properties, but to harness them, most clusters will have to be deposited on surfaces, where interactions between them and their substrates may alter the clusters' original properties. Thus, it is important to determine how the intrinsic properties of clusters are changed by surface interactions. The goal of this project is to measure the properties of free (gas phase) clusters and those same properties of the same cluster sizes and compositions deposited on various substrates. Our project focuses on measuring the properties of both free (gas phase) and surface-supported (soft-landed) clusters, using anion photoelectron spectroscopy and surface analytic techniques (STM, AFM, XPS, UPS, and Auger spectroscopy), respectively. In the surface-oriented experiments, cluster anions of materials science interest are generated by a magnetron sputter source, transported by ion optics through a sector magnet where they are mass-selected, and soft-landed on a waiting surface in an ultra high vacuum target chamber. There, they are subjected to analysis by the techniques mentioned above so that comparisons can be made with their free (gas phase) properties. The project title was changed in our most recent proposal to “Size-Selected Clusters on Surfaces” to better reflect the broader goals of the project.

FY 2012 HIGHLIGHTS

We have utilized STM imaging and XPS to study the structural evolution of “baby crystal” cuboids, including those of lead sulfide, on their way toward forming bulk crystal structures. We have also used AFM to study novel fractal patterns due to the deposition of partially oxidized, titanium nitride clusters. In addition, we have begun to expand our experimental capabilities to study cluster catalysis and reactivity on surfaces.

Emerging Functionality in Transition-Metal Compounds Driven by Spatial Confinement

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Funding:	$380,000

PROGRAM SCOPE

The exotic properties displayed by correlated electronic materials such as the cuprates, manganites, ruthenates, Fe-based penictides, 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, x-ray diffraction, and electrical and magnetic transport measurements will be conducted ex situ. We will look at complex doped manganites, ruthenates, and nichelates 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 break down. 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 magnetic nano-clusters. Strain also gives a non-thermal parameter to be used 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 2012 HIGHLIGHTS

In insulating oxide heterostructures such as $LaAlO_3/SrTiO_3$, a metallic or superconducting state can arise at the interface. Conversely, ultrathin films of metallic oxides can become insulating at reduced scales. The question of what drives these phenomena is one of the most hotly contested questions in condensed matter physics at this time, with contrasting camps attributing it to either an intrinsic effect caused by dimensional confinement or a chemical effect caused by the interfacial bonding, segregation, impurity doping, or stoichiometry. We are making progress on answering this question by systematically studying the thickness-dependence of the structure/property relationship in thin crystalline films of $La_{2/3}Sr_{1/3}MnO_3$ (LSMO) grown with UHV pulsed laser deposition on $SrTiO_3(001)$. In these systems, the material is nominally metallic at thicknesses greater than 3-4 nm and insulating in thinner samples. By minimizing the oxygen deficiency and other extrinsic effects, we have found the intrinsic critical thickness, structural relaxation, as well as the related surface effect of the dead layer. Thus we are gaining further insight into the emergent electronic phenomena brought on by broken symmetry and reduced dimensionality of oxide materials. These findings have been well received in the basic science community and should prove fruitful in transitioning these materials to practical applications.

Interfacial Thermal Resistance of Carbon Nanotubes

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PROGRAM SCOPE

This project seeks to develop new nanoscale thermal imaging techniques utilizing electron microscopy and to use these techniques to study thermal transport in carbon nanotubes. Through the course of the project, we are developing a thermal imaging technique called electron thermal microscopy that leverages the melting transition of low-melting-point islands to obtain thermal maps around a nanoscale region of interest. Using this technique, we are studying the thermal transport in carbon nanotubes. Results from the project have already shown that nanotubes have a high thermal contact resistance with a dielectric substrate, which is a surprising result, given the high intrinsic thermal conductivity of nanotubes themselves. By exploring different nanotube interfaces under different physical conditions, we seek to understand the mechanisms that govern this thermal interface resistance and how to control them. The outcome could result in a higher degree of control in the thermal management of materials at the nanoscale and also perhaps guidance for producing new high performance thermally conducting materials based upon engineered nanotube composites.

FY 2012 HIGHLIGHTS

During the project period, a manuscript was accepted for publication in *Nature Nanotchnology* [Kamal H. Baloch, Norvik Voskanian, Merijntje Bronsgeest, and John Cumings, Remote Joule heating by a carbon nanotube, *Nature Nanotechnology*, 7(5), p. 316 (2012)]. Graduate student Norvik Voskanian is working on observing the thermal transport from crossed nanotubes into substrates. The geometry should allow to differentiate the thermal transport between nanotubes from the thermal transport into substrates. Mr. Voskanian is also working to thermal bias the substrates so the thermal transport can be imaged at low applied power. During the award period, Dr. Kai He joined the project to perform electron holography observations of nanotubes under transport conditions. This should allow simultaneous imaging of the electrostatic potential drop (showing the regions of electrical dissipation) as well as the temperature distribution (showing the regions of dissiapation). Correlations of such results should allow the further determination of the origins and mechanisms of thermal dissipation in current-carrying nanotubes.

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:	$150,000

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 alkaline anion 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 2012 HIGHLIGHTS

This project was active during the last three months of Fiscal Year 2012. During this time, we have successfully developed a methodology to perform 2-dimensional characterization of fuel cell membranes using multifrequency AFM combinations based on frequency- and amplitude-modulation techniques. We are now able to carry out repeatable routine measurements both using regular scanning patterns as well as volume scanning methods. We have also made progress in developing a more quantitative interpretation of the factors governing measurement contrast in liquid environments through the implementation of atomic-resolution imaging procedures for crystal surfaces. This allows us to tune the image contrast so that different types of features, such as defects or adatoms, are visible under different sets of imaging conditions.

Dynamical Nanoscale Crystallography with Femtosecond Resolution

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PROGRAM SCOPE

Imaging the transformation of materials at combined atomistic spatiotemporal resolution (femtosecond-picometer) is at the forefront of the modern development of microscopy. Such realization will offer a glimpse into the dynamics of nanoscale materials undergoing transformation at the most fundamental level, thereby impacting our understanding of how to manipulate matter on the nanometer scale. Employing femtosecond electron pulses and laser pulses in a pump-probe sequence, it is possible to reconstruct the transient atomic structures by way of modeling the electron diffraction pattern from optically excited nanostructures on the femtosecond timescale. In this proposal, we would like to pursue two directions of significant scientific and technological interests: optical control of matter and time-domain study of transport in nanostructures. For the former, we will investigate low-dimensional solids with intrinsic lattice distortion (Peierls distortion) at the ground state. In such materials, it is possible to directly influence their global structural or electronic order by optical excitations. For the latter, we will conduct spatiotemporally resolved electronic and thermal transport measurements in nanostructures with our ultrafast diffractive potentiometry setup to understand some of the peculiar phenomena that are thought to be intrinsic to nanoscale. These mechanisms are generally difficult to be investigated with steady-state method or ultrafast optical techniques. Only through the sensitivities on both electronic and thermal energy transport can we elucidate such nanoscopic nonequilibrium processes relevant for the development of future electro-optical nanodevices.

FY 2012 HIGHLIGHTS

We have evaluated three essential space-charge-led features: the pulse lengthening (Coulomb explosion) following a power-law scaling growth, the broadening of the initial energy distribution, and the virtual cathode threshold—and discussed their roles in the proposed setup of a new RF-enabled high-brightness ultrafast electron microscope. Using femtosecond electron crystallography, we provided an atomic perspective on the ultrafast dynamics in the melting and reconstitution of charge-density wave. These atomically resolved dynamics provide a framework to understand the unique electron-phonon mechanisms driving the formation of different charge-density wave systems. Using optical, TEM, and ultrafast electron diffraction experiments, we have investigated the mechanism of a structurally coupled metal-insulator transition in VO_2, where a new monoclinic metal phase that lies between the insulating monoclinic phase and the metallic rutile phase has been identified, suggesting that metal-insulator transition might be classified as Mott-driven, Peierls-limited.

Electronic States and Transport in Semiconductor Nanostructures

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Funding:	$155,000

PROGRAM SCOPE

The understanding of electronic states and transport through dimensionally-confined semiconductor structures is a classic problem in materials physics. Advances in experimental probes and computational methods have led to several important breakthroughs including lattices of quantum dots (QDs) and accurate electronic structure models for nanostructures. Yet, a number of critical fundamental questions regarding the effects of QD size, spacing, and arrangements on the electronic states and transport through semiconductor nanocomposites remain unanswered. For example, *How many atoms are needed in a QD for it to cross over from behaving as an impurity state to a band of states? How do point defects and dopants influence the band structure, the positions of confined states, and transport through ensembles of QDs? How do interface disorder and strain affect the QD electronic states and transport through QD nanocomposites?* The program combines leading edge experimental and computational methods to answer these questions and develop a set of design rules for predicting the electronic states and transport in semiconductor nanocomposites.

This program seeks to understand electronic states and transport in dimensionally-confined semiconductor structures. Specifically, the effects of nanostructure size, spacing, and arrangement; strain and interface disorder; and the presence of point defects and dopants on the electronic band structure, confined states, and transport will be investigated using a novel combination of state-of-the-art experiments and theory. Using the probe tip of a scanning tunneling microscope, electronic spectroscopy measurements with nanoscale spatial resolution are performed on precisely fabricated QD nanocomposites. The imaging and spectroscopy measurements are performed over a wide temperature range, thereby facilitating measurements of the influence of magnetic dopants on nanostructure confined states and the probing of transport properties over a wide range of electron-phonon scattering conditions. Simultaneously, electronic structure based calculations of confined states and electron transport will be performed using experimentally-determined QD morphologies. Comparisons between experimental and computational studies will reveal both the origins of the electronic states and transport properties in semiconductor nanostructures, as well as the validity of the physical assumptions underlying the experimental and computational techniques.

FY 2012 HIGHLIGHTS

We use cross-sectional scanning tunneling microscopy, scanning tunneling spectroscopy (STS), atom-probe tomography, and OrderN Tight Binding [O(N)TB] to examine the influence of atomic structure on confined states in InAs:GaAs, InAs:Mn/GaAs, and GaSb/GaAs QDs. We demonstrated enhanced near-IR absorption due to the presence of InAs QD in a GaAs p-i-n structure. STS reveals Type I band offsets in GaSb/GaAs clusters grown on both As- and Sb-terminated GaAs surfaces. We developed a Fourier heat conduction model for quantifying thermally induced electron transport measurements. We developed a combined atomistic/continuum model to study electron transport in InAs QDs in GaAs p-i-n structure.

Structure and Dynamics of Domains in Ferroelectric Nanostructures – In-situ TEM Studies

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Funding:	$175,000

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 TEM holder which allows the direct observation of nucleation and dynamic evolution of ferroelectric domains under applied electric field. Specifically, we propose to (1) study the roles of static electrical boundary conditions and electrical charge in controlling the equilibrium domain structures of $BiFeO_3$ thin films with controlled substrate constraints; (2) explore the fundamental mechanisms of ferroelectric domain nucleation, growth, and switching under an applied electric field in both uniform thin films and nanofabricated nanostructures; (3) understand the roles of crystal defects such as dislocations and interfaces in these processes; and (4) 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 2012 HIGHLIGHTS

We have extensively explored nanoscale ferroelectric switching phenomenon using the techniques, equipment, and software analysis tools previously developed under this project. For the first time, we have directly observed nanoscale ferroelectric switching in real-time and studied the rapid formation of nanometer-scale ferroelectric domains by an applied electric field in TEM. Such ferroelectric domains can serve as memory “bits” similar to current magnetic memories but potentially with much higher densities. This breakthrough was made possible by a novel in situ scanning probe built in a TEM holder which enables one to apply an electric filed across a cross-sectional specimen while domain structures are imaged in TEM. From watching the polarization switching in two prominent ferroelectric materials, we were able to study the underlying nucleation and growth mechanisms. We found that neither material strictly followed the contemporary model of domain nucleation and growth. One reason for this deviation is frequent episodes of domain pinning whereby the domain growth was slowed or stopped as it impinged on defects. Our work on the dynamics of ferroelectric domains has been published in several journals, including *Science* 334, 968 (2011) and *Nat. Commun.* 2:591 doi: 10.1038/ncomms1600 (2011).

Study of Energy Transport at the Nanoscale

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Funding:	$136,000

PROGRAM SCOPE

The goal of this project is to probe the novel transport phenomena that occur in nanometer-sized molecular junctions (MMMJs) due to the confinement of phonons and electrons in them. While some progress has been made in understanding energy transport in MMMJs, the thermoelectric properties, heat dissipation characteristics, and spin dependent charge transport properties of MMMJs remain largely unexplored due to the lack of the required experimental tools. In order to achieve this goal, we will develop both novel scanning probes with integrated thermocouples and microdevices that can resolve small heat currents. Using these platforms, we will perform experiments on a variety of MMMJs to elucidate the effect of molecular structure and magnetization direction of electrodes on (1) the Seebeck coefficient, (2) phonon transport properties, and (3) energy dissipation in MMMJs. Answering these questions will not only elucidate the dependence of energy and charge transport properties on the structure of MMMJs, but will also provide important information on the electronic structure of molecular junctions and electron-phonon interactions in them. Further, these experiments will provide much needed data to advance physical theories that describe nanoscale transport.

FY 2012 HIGHLIGHTS

We have successfully accomplished the goal of developing scanning thermal probes with integrated thermocouple probes that are compatible with operation in an ultra-high vacuum (Kim *et al.*, ACS Nano, 2012) and have also developed the tools to measure ultra-small heat currents (Sadat *et al.*, Appl. Phys. Lett., 2011). By leveraging these tools, we have recently probed heat dissipation at the molecular scale and have identified that heat molecular scale heat dissipation is intimately related to the electron transmission characteristics of MMMJs. These novel effects have been described in a manuscript that is currently under review. Further, this project has also successfully elucidated the relationship between Seebeck coefficients and molecular structures (Tan et al., JACS, 2011).

Nanoscale Resistive Switching Behavior of Ferroelectric and Multiferroic Tunnel Junctions

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Funding: $250,000

PROGRAM SCOPE

The main objective of the proposed research is the experimental implementation and demonstration of polarization-controlled tunneling resistance switching using a combination of high-quality epitaxial oxide heterostructures and advanced scanning probe microscopy (SPM) characterization supported by first-principle calculations of the resistive states in these heterostructures. A set of SPM techniques will be employed to study the critical and switching behavior in ultra-thin (several unit cells) heterostructures in conjunction with their transport properties. Single-crystal epitaxial heterostructures will serve as model systems for experimental SPM studies. The first-principle modeling using density-functional calculation schemes will focus on predicting the critical behavior and transport properties of FTJs and MFTJs.

FY 2012 HIGHLIGHTS

Recently, we have demonstrated that the nonvolatile tunnelling electroresistance (TER) effect in ultrathin (several nanometer-thick) ferroelectric films could be induced by purely mechanical means and showed that this effect could be realized without any involvement of surface electrochemical processes commonly expected in SPM poling of oxide films. Comparison between electrically- and mechanically-induced TER effects allows assessment of the surface charge influence on resistive switching.

We have also demonstrated memristive behavior in FTJs, where the tunneling conductance can be tuned in an analogous manner by several orders of magnitude by both the amplitude and duration of the applied voltage. The ferroelectric tunnel memristors exhibit a reversible hysteretic nonvolatile resistive switching with resistance ratio of up to 10^5% at room temperature. The observed memristive behavior is attributed to the field-induced charge redistribution at the ferroelectric/electrode interface resulting in the modulation of the interface barrier height.

Discovery of Dielectric Response and Forces in Sub-Nanoscale Objects

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Funding:	$200,000

PROGRAM SCOPE

We wish to explore the optical dielectric response of sub-nanoscale particles on technologically important substrates, using inelastic scattering of a sub-Ångstrom fast electron beam. This information will be useful for understanding reporter-molecule/particle structures designed for Surface Enhanced Raman Scattering; surface plasmon amplification and stimulated emission in metal/dye composite structures; electrical contact behavior using metal islands on graphene, graphene oxide, and other molecular objects; and carrier separation in photo-voltaic structures. In graphene structures, groups of metal islands may be evaluated for carrier plasmon confinement cavities. We also wish to understand inter-object forces, the strength of near and far-field photonic coupling, and possible unanticipated optical behavior in molecular and nano-scale objects. This project includes a wide range of activity: (1) preparation of practical sub-nanoscale objects and substrates, (2) Ångstrom-level structural imaging and electron energy loss spectral (EELs) analysis, (3) exploration of dielectric response theory to understand observed behavior, and (4) development of new EELS detector capability for surface plasmon spectral analysis at optical frequencies.

FY 2012 HIGHLIGHTS

Dr. M. J. Lagos (hired in October 2011) has set up equipment for preparation of very small metal particles (Au, Pt, Cu, and lately, Al), first in a dedicated vacuum system and then in the VG-scanning transmission electron microscope (STEM) airlock to help control oxidation of reactive materials. He established collaborations with the groups of Chhowalla and Andrei at Rutgers to produce single layer graphene substrates appropriate for electron microscopy. This work has an important discovery component for collaborators in its emphasis on elimination of organic material, normally unimportant in measurements of bulk electronic behavior, which obscures the underlying graphene structure in microscopy. We have reproduced Ångstrom-level performance in the aberration-corrected VG STEM, after its move to Rutgers, using Au nanoparticles on graphene specimens made at Rutgers. This has been challenging, given the 30-year age of the system and on-going laboratory construction. The theoretical effort is concentrating on understanding the apparent repulsive dielectric force observed for very small impact parameters in 1-1.5 nm Au particles. Although modeling of the experimental scattering geometry has allowed us to frame the conditions under which it occurs, a detailed understanding of the underlying physics is elusive. We have begun to explore simpler models (with J. Aizpurua in San Sebastian) that capture the essential physics, in order to clarify the behavior. The detector development is about 70% finished, with delivery of a windowless sCMOS detector, fiber optic coupling, and scintillator-ready fiber optic vacuum windows. During this year, this work has resulted in three invited presentations (one international) and two archival journal publications (including one invited review).

In Situ Scanning Force Microscopy Studies of Cross-Coupled Domains and Domain Walls

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Funding:	$150,000

PROGRAM SCOPE

The objectives of this project are 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 2012 HIGHLIGHTS

This is a new project funded by DOE starting July 1, 2012. We have successfully observed magnetoelectric response of cross-coupled domains in multiferroic hexagonal $ErMnO_3$, which demonstrates the feasibility of magnetoelectric force microscopy proposed in the proposal. Furthermore, we discovered emergent giant magnetoelectric response at the metamagnetic phase transition approaching zero temperature, suggesting a quantum-critical-like enhancement. In the next period, we will perform systematic studies of giant magnetoelectric response in multiferroic $ErMnO_3$ to understand the mechanism of magnetoelectric effects. We will also apply this powerful technique to other magnetoelectrics for visualizing cross-coupled domains and domain walls.

Nanoscale Properties of Novel Materials

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Funding:	$200,000

PROGRAM SCOPE

The goal of this project is to use a combination of nanoscale patterning, transport measurements, and multimode scanning probe techniques to investigate the properties of novel materials, in particular structures fabricated from epitaxial thin films of complex oxides using pulsed layer deposition (PLD).

Complex oxides are fascinating materials with almost identical crystal structure but with widely divergent functionalities. This enables the growth of lattice-matched epitaxial structures consisting of layers of materials with different properties with atomically sharp interfaces, for example, superconductors in contact with ferromagnets, or ferroelectrics in contact with ferromagnets. Our focus is on understanding the interaction between the different order parameters present in these structures. In the past, we have investigated artificial multiferroic structures incorporating ferroelectric and ferromagnetic components and superconductivity in the new iron-based high temperature superconductors, the ferropnictides, using point contact spectroscopy. Our current focus is on investigating the properties of the two-dimensional electron-gas that forms at the interface between the two band insulators, lanthanum aluminate (LAO) and strontium titanate (STO). The project involves the development of scanning probe microscopes for use in extreme environments, in particular at millikelvin temperatures and high magnetic fields.

FY 2012 HIGHLIGHTS

Last year, we demonstrated, for the first time, the coexistence of ferromagnetism and superconductivity at the LAO/STO interface. This year, we showed that this coexistence of superconductivity and ferromagnetism allows for a unique manifestation of charge-vortex duality in the superconductor-to-insulator transition that is seen in this system.

New Methods of Imaging Surfaces

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Funding:	$160,000

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 proposal 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 U.S. This will involve both development of 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 kinetic factors determining which surface structures form. For instance, with an oxide supported catalyst or an oxide which is itself used as an active catalyst, knowledge of the detailed atomic structure of the surface as well as its chemical composition, thermodynamics, and kinetic factors is needed to fill the gap between structure and performance, paving the way for better catalysts to be engineered. A longer-term and somewhat ambitious 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, including information such as the atomic structure of surface steps, domain boundaries, and possibly even surface point defects. In addition to the above, a smaller effort will be continued on precession electron diffraction, primarily a collaborative development of a fast refinement approach.

FY 2012 HIGHLIGHTS

In the initial period of the project, we have obtained good data for the $SrTiO_3$ (111) and (001) surfaces, and are in the process of inverting the images, combining this data with diffraction data, and performing DFT calculations.

Microscopic Subsurface Characterization of Layered Magnetic Materials using Magnetic Resonance Force Microscopy

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Funding:	$190,000

PROGRAM SCOPE

Our novel FMR Imaging technique is well suited to local studies of ferromagnetic mode dynamics and spin wave transport. Our objectives are to gain improved and integrated understanding of two interrelated phenomena; we seek to better understand the microscopic mechanisms that underlie spin pumping and to gain improved insight into the role of spin wave emission and spin wave transport in spin pumping and in damping of the precessing ferromagnetic magnetization.

Our research program builds on a unique constellation of experimental capabilities and experience available in the proposer's laboratory. At the foundation of the program, is a novel technique (nearly unique—this technique has recently been reproduced by the NIST group) that we have developed [Lee et al., Nature (2010)] known as Ferromagnetic Resonance Imaging (FMRI); this provides microscopic mapping and spectroscopic characterization of static and dynamic properties of ferromagnets with sub-200-nm spatial resolution and field resolution of 1 Gauss in a 1-Hz bandwidth.

FY 2012 HIGHLIGHTS

We have made several advances in microscopically resolved, scanned probe subsurface studies and imaging of multicomponent magnetic materials:

- Studies of magnetic systems with exchange bias using Ferromagnetic Resonance Force Microscopy (FMRFM) including spectroscopic mapping of the internal magnetic fields and investigation of interface influence on the localized mode shape

- Demonstration of a capability for tuning magnetic anisotropy in ferrimagnetic double perovskite films by tuning the stress induced by material lattice mismatch with the substrate
- Development of a novel method to image spin properties of spintronic systems using the spatially varying magnetic field of a scanned micromagnetic probe in conjunction with existing electrical or optical global spin detection schemes
- Investigation of the physical properties, including anisotropy and field-sensing bandwidth, of self-biased Bismuth-substituted rare-earth iron garnet films
- Demonstration of a method of quantitative magnetic force microscopy in a strong magnetic field

The advances and accomplishments of this research period, including extensive research data, analytical and micromagnetic analysis, modeling of observed phenomena, and the discovery of underlying mechanisms and applications of these advances to microscopic studies of technologically and scientifically important materials, have been presented in 9 publications.

Spin-Polarized Scanning Tunneling Microscopy Studies of Nanoscale Magnetic and Spintronic Nitride Systems

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Funding:	$80,000

PROGRAM SCOPE

This DOE-sponsored project has two important goals: (1) probe the fundamental electronic and magnetic properties of technologically-promising bilayer systems consisting of an atomic layer of magnetic material on top of a layer of nitride semiconductor material, and (2) firmly establish a strong U.S.-led research effort in the field of spin-polarized scanning tunneling microscopy (SP-STM). In the project, magnetic/spintronic nitride bilayer systems are synthesized using the technique of molecular beam epitaxy and/or pulsed laser epitaxy in which the properties of the growing surface are carefully tailored by monitoring the process via *in-situ* reflection high energy electron diffraction. Using this method, it is possible to create magnetic nitride layers of all types—ferromagnetic, antiferromagnetic, and spintronic layers involving dilute magnetic doping. Another important aspect of the project looks at correlated properties, including correlations between nanometer scale surface structure and the electronic and magnetic properties.

In fulfilling the second objective, PI Smith draws upon a decade of experience in the field of SP-STM. In this technique, a sharp needle-like, metallic probe with an ultra-thin magnetic coating is brought to within a few atomic diameters away from the sample surface of interest. As the tip scans across the surface, the tunneling current between tip and sample responds to minute changes in the magnetic conductance of the tip-sample junction. These minute variations then yield a two-dimensional mapping of the magnetic spin structure of the surface. Application of a magnetic field during this process provides additional information by polarizing either the tip or sample magnetization, thus enabling both in-plane and out-of-plane sensitivity.

FY 2012 HIGHLIGHTS

The PI's group has made several key accomplishments relating directly to the two main stated objectives. First of all, one paper published in *Applied Physics Letters* details the discovery of quantum height MnGa islands formed via a spontaneous process on gallium nitride surfaces. The next step is to determine the detailed crystalline structure and magnetic properties of these islands. Second, a paper has been published in *Nano Letters* which details the discovery of an unexpected orthogonal magnetic anisotropy occurring on the stepped surfaces of manganese nitride spin pyramids; in this study, the power of SP-STM was fully utilized in order to map out the novel magnetic ordering. And thirdly, in a paper published in *Journal of Applied Physics*, a unique method has been demonstrated for embedding an atomic layer of manganese atoms in a gallium nitride thin film, which may lead to the possibility of magnetic delta-doped, spintronic gallium nitride.

Structure and Dynamics of Domains in Ferroelectric Nanostructures - Phase Field Modeling

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Funding:	$143,000

PROGRAM SCOPE

This program is focused on investigating the basic science of domain structures and dynamics in ferroelectric thin films and nanostructures using the phase-field method, in close collaboration with experimental groups using high resolution transmission electron microscopy, in situ TEM with scanning probe microscopy, or piezoresponse force microscopy. The main objective is to fundamentally understand the electromechanical effects on ferroelectric domain stability and on mesoscale domain switching mechanisms by close integration of computer simulations and experiments. The primary material systems to be studied are $BiFeO_3$ and related oxides. $BiFeO_3$ is one of the most promising single-phase candidates for magnetoelectric device applications due to the coexistence of ferroelectricity and antiferromagnetism at room temperature. Specifically, the program is aimed to (1) develop the modeling capability of three-dimensional (3-D) ferroelectric domain evolution with spatial distributions and transport of charged defects; (2) study the fundamental roles of electric boundary conditions, film thickness, and strain in the formation of ferroelectric and ferroelastic domain structures; and (3) investigate the interactions between domain walls and charged defects as well as their influence on switching mechanisms, remnant polarization, and coercive field.

FY 2012 HIGHLIGHTS

In collaboration with Pan's group at University of Michigan, we predicted, through phase-field simulations, that the domain structure under short-circuit boundary conditions formed (101)-oriented domain structures while the open-circuit domain structures formed (010)-oriented domains to reduce the bound charge at the film/substrate interface. It was discovered that small triangular nanodomains, formed at the domain/domain/substrate and domain/domain/surface interfaces in the open-circuit case, result primarily from the minimization of electrostatic energy. These nanodomains may be important for controlling in-plane switching in rhombohedral ferroelectric thin films as they represent spontaneous backswitched regions.

In collaboration with Kalinin's group at Oak Ridge National Laboratory, we studied the properties of topological defects, i.e., junctions of four polarization variants, forming a 1-D wall through the thickness of the film. Our phase-field simulations demonstrated that the experimentally observed much higher-than-usual electrical conduction is a result of high electrostatic/elastic fields at these defects which contribute to segregation electronic/ionic charges. These defects offer a path towards writable/rewritable nanoelectronics, in which we can control the conductive paths of a film through domain structure control.

Local Electronic and Dielectric Properties at Nanosized Interfaces

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Funding: $135,000

PROGRAM SCOPE

The goal of this project is to determine the origin of the properties of nanosized interfaces through several complementary approaches: direct probe of size dependent metal/oxide interfaces electronic properties, development of local probes of dielectric properties, and in situ probes of properties in energy related devices.

FY 2012 HIGHLIGHTS

The most promising strategies for addressing global energy challenges rely on complex materials systems (solar cells, batteries, super capacitors, and fuel cells) that contain multiple compounds, interfaces, and junctions. Device functionality often involves dynamic electrochemical interactions occurring in extreme environments. Solid oxide fuel cells (SOFCs), for example, comprise a series of several dissimilar materials and phases in contact (cathode/electrolyte/anode)(*3-6*) and operate at 500-1000°C in reactive gaseous environments, directly converting chemical energy into electrical energy and heat. We have developed a method for direct, local imaging of electrochemical phenomena occurring at electrode-electrolyte interfaces of operational symmetrical fuel cells using in-situ scanning probe microscopy.

Strontium (Sr)-doped lanthanum manganite (LSM) is one of the most commonly used perovskite materials for SOFC cathodes, essentially behaving as a pure electronic conductor, which limits SOFC cathode reactions to TPB regions. In contrast, in SOFC electrodes comprised of mixed ionic/electronic conducting (MIEC) electrode materials, such as Sr-doped lanthanum ferrite (LSF) and Sr-doped $LaCo_yFe_{1-y}O_3$ (LSCF), the reaction zone extends from the TPB into the electrode bulk. Therefore, we fabricated two symmetrical fuel cells: (LSF)—yttria-stabilized zirconia (YSZ) and (LSM)—YSZ cells to enable direct comparison between the expected electrochemical processes of electronic conducting and MIEC electrode materials.

At 600°C sharp, linear potential variations indicate interfacial space-charge regions. The active zone and triple phase boundary widths are mapped, and important parameters such as activation energies and diffusion coefficients are estimated. This scanning probe approach demonstrates, for the first time, direct imaging of local interfacial potential perturbations across electrode-electrolyte interfaces. By comparing fuel cells based on two common electrode materials, we also demonstrate the ability to image and distinguish between bulk-mediated and surface mediated transport mechanisms.

Electron Density Determination, Bonding and Properties of Tetragonal Ferromagnetic Intermetallics

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PROGRAM SCOPE

The unique properties of chemically ordered intermetallics are often superior to those of elemental metals and compositionally equivalent solid solution alloys, rendering them suitable for various high-performance applications. This project combines transmission electron microscopy (TEM) based quantitative convergent-beam electron diffraction (QCBED) experiments with accompanying electronic structure calculations by density functional theory (DFT) to study the electron density and interatomic bonding in transition metal based intermetallics. The methods developed here focus on measuring the electronic charge difference distribution, $\Delta\rho(r)$, as one of the quantum mechanical characteristics central for developing fundamental understanding of crystal properties. $L1_0$-FePd and $L1_0$-FePt are selected as the primary model systems for 3d-4d/5d electron interactions. Other transition metals and intermetallics are used to evaluate effects of ferromagnetism on the QCBED methods. Establishing robust, accurate, and facile methods for probing experimentally the electron density, $\rho(r)$, in crystals, which is a direct result of DFT calculations, remains a high impact goal. This effort advances the state of the art in quantitative TEM experimentation, provides new experimental data uniquely suited for evaluation of DFT approximations, and enables development of improved DFT tools for intermetallics based on elements with atomic numbers beyond Si.

FY 2012 HIGHLIGHTS

High quality QCBED data, e.g., structure factors with $h^2+k^2+l^2 \leq 16$ and Debye Waller factors, have been obtained for Cu, Ni, Fe, Cr, FePd, and TiAl. Comparisons with of DFT calculations indicated that the low order structure factors with $h^2+k^2+l^2<5$ contain essentially all the details from interatomic bonding. For the intermetallics, DFT calculations based on LDA/VASP are not reliable beyond the second lowest structure factor, F_{110}, breaking down already for the strongly bonding affected F_{111}. In contrast, beyond-LDA Wien-2K based DFT (e.g., GGA-PBE) results exhibit excellent agreement with QCBED experiments for the transition metals Cr, Fe, Cu, Ni, and intermetallic $L1_0$-TiAl. GGA type DFT calculations consistently overcompensate for delocalization of electron charge. Differences between DFT calculations and QCBED experiment are mostly associated with d-electrons. Bloch-wave analysis indicated that the superior precision and sensitivity achieved with the multi-beam off-zone axis QCBED for simultaneous refinements of multiple Debye-Waller factors and multiple structure factors has been correlated with the increased number and increased amplitudes of excited Bloch wave branches. Equiatomic FePt and Pd-rich $Fe_{1-x}Pd_x$, $0.5<x\leq 0.58$, intermetallic alloys have been prepared by vacuum arc-melting.

Quantum Control of Spins in Diamond for Nanoscale Magnetic Sensing and Imaging

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Funding:	$150,000

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 2012 HIGHLIGHTS

Our paper in *Nature Nanotechnology* published earlier this year demonstrated the application of quantum phase estimation algorithms to improve DC magnetic field sensing with single spins in diamond. We have extended these results to fluctuating magnetic fields, and demonstrated significant improvement in sensing both amplitude and phase of AC magnetic fields. This work is now being written up for publication.

We are also building up a second confocal system that will be integrated with a custom-build scanning probe microscope for using diamond tips to sense magnetic fields from other samples containing spins. We are also evaluating the possibility of commercial systems.

High-Resolution Photoemission Electron Microscopy

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Funding:	$220,000

PROGRAM SCOPE

Photoemission electron microscopy (PEEM) is a unique microscopy method which is currently in extensive use in surface science, ultra-fast microscopy, and magnetism. PEEM combines photon probing with electron imaging. The imaging electrons originate from a photoemission process when the specimen is exposed to visible or higher energy light. Unique advantages of PEEM are a high surface sensitivity, which allows a probing of nanovolumes without extensive sample preparation and unique surface contrasts, which can be chemical, electrical, or optical in nature. PEEM also allows a large variety of photon-based spectroscopies to be implemented—among them, ultra-fast methods.

Our research group has designed and built an aberration-corrected photoemission microscope which currently has the highest spatial resolution available. In this project, we aim to further improve the resolution in PEEM by re-designing the aberration corrector and installing other electron optical components to increase image stability, contrast, and brightness. Concurrent with the instrument development, we carry out work on characterizing fast electronic processes at metal-dielectric interfaces. We use PEEM to directly visualize the intensity distribution and mode structure of surface plasmon polaritons in metal films using femtosecond light pulses. We study localized and propagating surface plasmons. We optimize plasmon generating structures for strong field enhancement and then study charge and energy transfer within the near-field region with highest available resolution.

FY 2012 HIGHLIGHTS

In the past year, we improved the spatial resolution to ~4 nm and installed an optical delay line which now allows stable time delays of light pulses down to approximately 200 attoseconds. These technical advances were used in the study of surface plasmons in gold nano-structures. Using femtosecond visible light pulses, we showed that near-field energy transfer between plasmonic and non-plasmonic materials can be quite significant and can result in strong localized photoemission at the interface between the materials. This photoemission is confined to areas smaller than ~25 nm and is highly polarization-dependent. The transfer of energy can be controlled by switching the polarization of the excitation light. We presented a simple plasmon-router structure with sub-micron dimensions. We also found that the energy transfer in and out of plasmonic receiver structures can be visualized in PEEM. At interfaces with dielectrics, we directly observed the excitation of various surface plasmon modes—among them, long-range modes with propagation distances reaching the micrometer range.

We are currently studying details of these energy transfer processes, particularly their efficiency limitations and coherence.

Probing Correlated Superconductors and their Phase Transitions on the Nanometer Scale

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Funding:	$100,000

PROGRAM SCOPE

This program will focus on understanding how correlated electronic states in materials with d and f electrons undergo phase transitions to form an unconventional metallic phase and the mechanisms by which these states become superconducting states with lower temperatures. Our aim is to provide a microscopic view of these exotic materials and their phase transition into the superconducting state by using scanning tunneling microscopy (STM) and spectroscopy techniques. These experiments will provide important evidence that will help constrain theoretical models of unusual normal states in these complex materials and their potential mechanisms for superconductivity.

This program will be divided into two parts. The first will focus on examining the properties of high-Tc cuprate superconductors and the high-temperature pseudogap phase of these materials. The second component will be to utilize STM techniques to study the exotic normal and superconducting phases in heavy fermion compounds. The parallels between the puzzles in heavy fermions and cuprates suggest that heavy fermions might provide important clues into understanding correlated electrons and their superconductivity. Similar to the high-temperature superconducting cuprates, understanding the mechanism behind the unconventional superconductivity requires understanding the “normal state” prior to formation of superconductivity. The heavy fermions offer clean materials systems to examine issues that might be difficult to explore in the cuprates and new Fe-based superconductors due to doping disorder in those systems. In particular, the issue of proximity to a quantum critical point and the impact of quantum phase transition on the electronic properties of material and mechanism of superconductivity can be precisely probed in heavy fermion systems. The two components of the proposed program provide a broad attack on some of the most important problems in the physics of correlated materials and the emergence of superconductivity in these systems. Finally, the program will support the development of spin polarized STM measurements of correlated systems that can complement other STM measurements to directly probe the spin textures in such systems.

FY 2012 HIGHLIGHTS

We made an exciting advance in the study of heavy fermion compounds by using spectroscopic mapping with the scanning tunneling microscope to detect the emergence of heavy excitations upon lowering the temperature in a prototypical family of Ce-based heavy fermion compounds, (Nature 2012). The Ce-based compounds are particularly exciting to work on as they show a remarkably similar phase diagram to high-temperature cuprate superconductors. Additionally, we constructed a spin-polarized STM capable of performing spin resolved experiments on correlated materials. We were able to prepare clean metal samples in situ and obtained the first STM images with this machine at 1.2K. In the coming months, we will install evaporators for in situ preparation of magnetic atoms, so as to prepare spin-polarized tips, and to perform the first spin-polarized STM experiments.

Atom Chip Microscopy: A Novel Probe for Strongly Correlated Materials

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Funding:	$255

PROGRAM SCOPE

The goal of this project is to demonstrate the use of atom chips—substrates supporting micron-sized current-carrying wires that create magnetic microtraps near surfaces for thermal or degenerate gases of neutral atoms—to enable single-shot, large area detection of magnetic flux at the 10^{-6} Phi_0 level and below. By harnessing the extreme sensitivity of atomic clocks and Bose-Einstein condensates (BECs) to external perturbations, optimized atom chip technology could provide a magnetic flux detection capability that surpasses all other techniques by a factor of 10^2--10^3.

In addition, atom chip microscopy introduces three very important features to the toolbox of strongly correlated material microscopy: the simultaneous detection of electric fields down to the sub-single electron charge level; freedom from 1/f flicker noise at low frequencies, which plague scanning SQUIDs; and the complete decoupling of probe and sample temperatures. The first of these features will play an important role in studying the interplay between magnetic and electric domain structure in, e.g., multiferroic materials such as $TbMnO_3$. The last two are crucial for low frequency magnetic noise detection in the cuprate pseudogap region and for precision measurements of current flow—at the high temperature, technologically relevant regime inaccessible to other techniques—in manganites exhibiting colossal magnetoresistance strongly correlated insulators, such as vanadium dioxide, and 2D electron gases. This program will demonstrate the viability of atom chip microscopy for probing technologically-relevant strongly correlated materials and the percolation dynamics of the states of mixed phases therein.

FY 2012 HIGHLIGHTS

We have demonstrated the ability to rapidly create Rb BECs and trap them within microns of a surface in a cryostat containing the atom chip. The cryostat can be cooled to 30 K; and in the next period, we will demonstrate the feasibility of using atom chips with a BEC to image transport features on a cryogenically cooled surface containing a test wire pattern. Successful demonstration, in future cycles, will lead directly to the use of system for studies of transport in exotic and technologically relevant materials such as cuprate superconductors and topological insulators. We published a Phys. Rev. B paper this period proposing how to use our cryogenic atom chip microscope to determine the surface-to-bulk conductivity of a topological insulator. This may be done in a relatively model independent fashion by imaging the flow of surface current around etched trenches.

Vortex Matter in Confined Superconductors and Mesoscopic Hybrid Heterostructures

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Funding:	$205,000

PROGRAM SCOPE

This program is aimed at understanding the fundamental features that underlie the behavior of vortices under confinement in mesoscopic superconductors, hybrid superconductor-normal metal (S/N), and superconductor-ferromagnet (S/F) systems.

Properties of superconducting materials differ greatly from the bulk properties when the size of the sample is small (comparable to the coherence length and the London penetration depth). The superconducting critical current density can be largely enhanced and the vortex configuration can be strongly influenced by the sample geometry. As a result of the confinement, the presence of the sample's boundary promotes the appearance of exotic vortex states, otherwise forbidden in bulk materials (such as giant vortex state or vortex molecules).

Moreover, transport and thermodynamic properties are very different when a superconductor is placed in proximity of a ferromagnet. Superconductivity is suppressed by exchange interaction and by electromagnetic interaction. New phenomena can arise either from the effect of the stray field on the superconductivity, such as the formation of vortex-antivortex pairs, or from the local coexistence of superconductivity and ferromagnetism, such as the existence of an oscillatory superconducting order parameter at the interface of the ferromagnet and superconductor (Fulde-Ferrel-Larkin-Ovchinnikov state).

FY 2012 HIGHLIGHTS

We have made significant advancement in the study of S/F structures magnetically coupled. We have verified the theoretical criteria for formation of vortex-antivortex pairs in S/F systems and visualized them, with low temperature scanning tunneling microscopy and magnetic force microscopy, in different S/F systems. Furthermore, we have visualized the nucleation of superconductivity in regions above the separation between adjacent magnetic domains (on length scales of the coherence length); and we have observed the switching of superconducting regions into normal state upon applying a magnetic field. Our results prove that such S/F structures are attractive model systems since they offer the possibility to control the strength of the superconductivity through an external magnetic field or through rearrangement of the magnetic domains.

Physics of Complex Materials Systems through Theory and Microscopy /EELS

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Funding:	$271,000

PROGRAM SCOPE

The main objectives of this research program are to (1) create an integrated simulation capability of electron-energy loss spectra (EELS), including both diffraction theory that describes the propagation of the electron beam of a scanning transmission electron microscope through the thin film and the detector and density functional theory for the calculation of core and valence excitation process, including interference effects (so far, the two objectives have been addressed almost exclusively by different communities, one community leaving out solid-state effects, the other leaving out diffraction and interference); (2) pursue calculations to interpret available Z-contrast and EELS data for particular materials systems using available and newly-developed theoretical tools; and (3) explore the use of time-dependent density functional theory to simulate advanced imaging techniques. Accomplishments in all three areas are described below.

FY 2012 HIGHLIGHTS

(1) We completed the integration of the new codes that incorporate solid-state effects in EELS calculations with existing codes that incorporate the simulation of beam focusing, its diffraction in the solid, and its detection at the detector for “core loss” EELS (core electron excitations). We applied the method to new data to demonstrate the method’s feasibility and potential. A paper was submitted for publication. We also began the coding for “low loss” EELS (valence electron excitations) and parallelized the codes.

(2) We combined density-functional total-energy and EELS calculations with available data by collaborators at Oak Ridge National Laboratory, Vanderbilt University, the University of California, Berkeley, and the University of Illinois, Chicago, and produced a number of papers. Topics include the origins of white light emitted by ultrasmall CdSe nanoparticles, highly localized excited states in graphene, plasmon enhancement at impurities in graphene, magic clusters embedded in graphene, the origins of increased Seebeck coefficient in thermoelectric $Ca_3Co_4O_9$ films, the structure of highly-strained $BiFeO_3$ thin films, and interface control of bulk ferromagnetic polarization.

(3) We pursued initial simulations of atto-second imaging.

Future plans are to further develop the new codes and use them to study complex materials systems.

Correlation of Bulk Dielectric and Piezoelectric Properties to the Local Scale Phase Transformations, Domain Morphology, and Crystal Structure

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Funding:	$180,000

PROGRAM SCOPE

This research program aims to provide fundamental understanding of the mechanisms controlling the piezoelectric response in lead-free systems by systematically studying the local domain and crystal structures, and their effect on physical properties. $(Na_{1/2}Bi_{1/2})TiO_3$-x%$BaTiO_3$ (NBT-BT) single crystals and textured ceramics of compositions close to morphotrophic phase boundary (MPB) and $K_{0.5}Na_{0.5}NbO_3$-x%$LiNbO_3$ (KNN) single crystals and [001]-grain-textured ceramics near polymorphic phase boundary (PPB) are used as a representative lead-free system. The nanoscale domain structure and its ferroelectric response are being studied as a function of electric field and temperature. These studies have led to identification of the phase transformational sequences in the MPB region, the presence of intermediate bridging phases, and the similarities and difference in the mechanism of enhanced piezoelectricity for both MPB and PPB Pb-free systems. The nano-structure as a function of composition and temperature is being investigated by scanning probe microscopy, TEM, and HRTEM. We have determined the domain distribution, how elastic compatibility amongst hierarchial domains enhances piezoelectric properties, and how oxygen tilts influence the phase transformational sequence and piezoelectric properties.

FY 2012 HIGHLIGHTS

Recently, we made direct observation of monoclinic nanotwins with coherent twin boundary planar in MPB composition of $N_{0.5}B_{0.5}TiO_3$-$BaTiO_3$ through detailed HRTEM investigations. The smaller size of nanotwins explains the high piezoelectric response and large strain in this system. A monoclinic distortion of the crystal structure was observed at the nanoscale, which, however, was compensated over larger length scales, resulting in an average phase with rhombohedral symmetry (collaboration with Oak Ridge National Laboratory). These results emphasize the generic role of nanotwins with reduced symmetry towards enhanced piezoelectric properties of MPB compositions. The short-range crystallographic distortions in NBT-BT can explain different phase transitions that have been reported for this material around the MPB.

Microstructure and domain structure play dominant roles towards controlling the magnitude of piezoelectric coefficient and hysteretic losses in perovskites. Brick-wall like microstructure with large grain size and small domain size can provide significant enhancement in the magnitude of piezoelectric coefficient. In order to investigate the role of domain size and microstructure, we developed $[001]_{pc}/[012]_{Rh}$ grain-oriented ceramics with large grain size and an electrical poling technique that resulted in varying domain size. The local switching characteristics across the grain-oriented region with the embedded template phase were studied using the switching spectroscopy piezo force microscopy technique. Local hysteresis loops were collected across a 40×100 matrix, which contained the template as well as the matrix; and switching parameters like imprint, switching polarization, and work of switching were mapped across the surface. The results confirmed that the texturing enhances the homogeneity of the polarization across the matrix, which thereby provides an additive effect promoting the low polar anisotropy.

Combined Microscopy Studies of Complex Electronic Materials

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Funding:	$180,000

PROGRAM SCOPE

The goal of the project is to further the understanding and control of certain important complex electronic materials by applying combinations of scanning microscopy and transport techniques while simultaneously achieving maximal control of all the sample conditions to which the properties can be very sensitive. It is essential that the samples be single crystals, small enough to consist of a single domain so that the measured properties are homogeneous. An apparatus has been developed allowing precise application of strain to such crystals while temperature, magnetic field, and vapor environment are maintained, combined with full access by scanning optics. A material in focus is vanadium dioxide, whose dramatic metal-insulator transition (MIT) at about 67°C holds potential as a fast optical switching. The MIT remains poorly understood after decades of bulk studies. It may be considered a paradigm of materials with strong electron-electron and electron-phonon correlations whose properties should be elucidated by our approach. Other materials of increasing interest are the two-dimensional semiconductors, namely bilayer graphene and transition metal dichalcogenides, in which the strong confinement, Dirac valleys, and strong spin-orbit coupling result in new electronic and optical phenomena. Collaborations allow ultrafast optics, x-ray, scanning-probe and electron microscopy measurements to be performed on individual micron-sized single-crystal samples.

FY 2012 HIGHLIGHTS

We have performed scanning photocurrent microscopy on individual VO_2 nanobeams at and around the MIT, revealing the thermoelectric nature of the photoresponse and the efficient (rapid) relaxation of carriers in the insulating phase to local thermal equilibrium. We have also carried out ultrafast scanning photocurrent measurements on graphene p-n junctions, finding that photothermal contributions and built-in-field effects compete in the photocurrent generation.

Imaging Point Defects with Quantitative STEM

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Funding:	$218,000

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 will attempt to image 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.

We will apply the methods we develop to problems arising from point defects in complex oxide materials relevant to solid oxide fuel cells. We will test the hypothesis that huge enhance in oxidation-reduction reaction kinetics report at the $La_{0.8}Sr_{0.2}CoO_{3-\delta}$ / $(La_{0.5}Sr_{0.5})_2CoO_{4-\delta}$ interface arises from Sr segregation from the $La_{0.8}Sr_{0.2}CoO_{3-\delta}$ to the first few atomic layers of the $(La_{0.5}Sr_{0.5})_2CoO_{4-\delta}$, enhancing the oxygen vacancy concentration and thus the oxygen diffusion kinetics. Then we will measure concentrations and spatial distributions of point defects in $La_{1-x}Sr_xMnO_{3-\delta}$ thin films, with special attention to defect clustering. These experiments require comparison to density-functional theory simulations from co-investigator Dane Morgan.

FY 2012 HIGHLIGHTS

We completed studies of doping and defects in *n*-type and *p*-type ZnO nanowires and thin films. In nanowires, we showed that Sb can create *p*-type conduction through a pattern of voids and decorated inversion domain boundaries. The same mechanism does not create *p*-type ZnO thin films. We demonstrated sub-picometer precision STEM imaging of robust crystals, GaN and Si, at extremely high electron dose. At 10 times lower dose, we obtained 3 pm precision images of nanoparticles, showing relaxation of atoms at surfaces, edges, and corners.

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

PROGRAM SCOPE

Nanostructured graphene presents exciting new research opportunities to address fundamental issues in condensed matter physics (e.g., the spin-polarized graphene edge states, chaotic graphene billiards, Aharonov-Bohm interference and strained induced pseudo magnetic field in graphene quantum dots (QDs)) that may potentially lead to exotic new functionalities and applications. The scope of this project is to explore these novel properties of graphene nanostructures with an integrated approach utilizing atomic resolution scanning tunneling microscopy (STM) and atomic force microscopy (AFM), and density functional theory (DFT) and tight-binding calculations.

To tackle these challenging tasks, a highly interactive team has been assembled, integrating the PIs' strengths in material synthesis and imaging (Li) and calculations (Weinert). The preliminary work has demonstrated the feasibility of our integrated approach involving atomic resolution STM and AFM imaging and spectroscopy, and DFT calculations. Continued DOE support will make these investigations possible. The successful execution of the research plan will expand our knowledge base of the exotic properties and potentially enhanced functionalities of epitaxial graphene on SiC, a material system that can significantly impact the fields of nano electronics and spintronics.

FY 2012 HIGHLIGHTS

We have shown that single layer trenches (and hence edges) on epitaxial graphene on Si-face SiC(0001) can be created by Fe nanoparticle (NP) assisted hydrogen etching in ultrahigh vacuum. The next step is to systematically investigate the atomic structure of the edges, particularly edge defects, using non-contact atomic-resolution AFM.

On epitaxial graphene grown on C-face SiC(000$\overline{1}$), we have found that it is highly strained. Consequently, QDs of a few to tens of nm in size form at the early stages of growth. In the next period, we will carry out atomic resolution STM imaging and spectroscopy, non-contact AFM, and calculations to determine the atomic structure and deformation of these graphene QDs.

3D Visualization of Emergent Behavior in Nanoscale Functional Heterostructures

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Funding:	$1,208,000

PROGRAM SCOPE

This research is focused around a single theme: three-dimensional in-situ visualization of the emergent behavior that is seen in patterned functional nanostructures and heterostructures as their dimensions are reduced to the nanoscale. We are focusing our research on understanding the complex energy landscape in heterostructure nanosystems whose building blocks show resistance switching, ferroelectric, ferromagnetic, and superconducting properties. Our aim is to obtain a fundamental understanding of domain behavior and charge transport properties in these nanostructures through control of the parameters that contribute to their energy landscape, such as interlayer coupling, geometric effects that lead to anisotropy, and the interaction between adjacent nanostructures. A variety of methods can be used to probe emergent behavior on a global scale, but in nanoscale materials, it is essential to be able to probe the local behavior, which can best be done through direct imaging as a function of external stimuli such as applied fields, temperature, and/or time. Our multi-modal approach involves an interwoven combination of aberration-corrected Lorentz transmission electron microscopy (ALTEM) and advanced scanning force microscopy to solve scientific questions related to the behavior of ferroic nanostructures. A particular focus of our effort will be on the use of three-dimensional analysis and imaging techniques that we have developed to visualize domain and transport behavior in nanostructures.

FY 2012 HIGHLIGHTS

Magnetic frustration in artificial spin ices arises when the system tries to minimize its magnetostatic interaction energy. We have used ALTEM to study the magnetic frustration behavior in individual islands and magnetic force microscopy to study the magnetization reversal process of entire lattices and thus gain an understanding of how to control magnetostatic interactions in square lattices. We visualized the fine structure of the magnetic induction around nodes obeying spin ice rules and those displaying a magnetic monopole defect structure. More recently, in collaboration with Prof. M. De Graef, we explored the magnetization reversal behavior of the lattices using ALTEM and MFM correlated with Monte Carlo simulation. This allowed us to develop a model for the reversal process that, for the first time, takes into account the true island shape and thus correctly accounts for their interactions.

We explored the effect of the surface potential on the surface free energy of single crystal TiO_2 resistance-switching oxide using electrostatic force microscopy in a cell filled with highly pure gas and under a positive tip bias, to prevent surface anodization. Quantitative measurement of the influence of ambient gas led us to develop a model in which the adsorbed oxygen molecules interact with oxygen vacancies at the TiO_2 surface and change the surface potential. These results provide important clues about the role of oxygen vacancies and adsorbed oxygen anions in the change of charge transport.

Spectroscopic Imaging STM & Complex Electronic Matter Studies

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Funding: $320,000

PROGRAM SCOPE

Davis' program focuses on (1) topological superconductivity and, more importantly, topological surface states in Sr_2RuO_4—the only known topological superconductor; (2) the search for new topological superconductors in CuBi2Se3 and Bi0.32Sb0.16Pb0.32Te0.2; (3) visualizing quantum critical electronic matter in heavy fermion compounds such as $YbRh_2Si_2$; and (4) high precision transport/thermodynamic measurements of novel and complex forms of electronic matter for example spin liquids and monopole fluids.

FY 2012 HIGHLIGHTS

Efforts made during Fiscal Year 2012 include (1) spectroscopic imaging STM studies of energy gap structure in topological superconductor in Sr_2RuO_4; (2) spectroscopic imaging STM studies of energy gap structure in what turned out to be non-topological superconductor $CuBi_2Se_3$; (3) measured density of electronic states within the quantum critical electronic matter in heavy fermion compound $YbRh_2Si_2$; and (4) development of new cryostat and instruments for high precision transport/thermodynamic measurements of spin liquids and monopole fluids.

Studies of Nanoscale Structure and Structural Defects of Advanced Materials

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Funding: $2,148,000

PROGRAM SCOPE

The overall goal of this program is to study the property sensitive nanoscale structures and defects of technologically-important materials such as superconductors, multiferroics, spintronics, and other energy-related materials including catalysts, thermoelectric, photovoltaic devices, and batteries. We develop and employ advanced quantitative electron microscopy techniques such as coherent diffraction, atom and spin imaging, atomically-resolved spectroscopy, and electron holography to study electrons, spins, orbitals, and lattice correlations as well as materials' physical and chemical behavior. We particularly emphasize gaining a detailed understanding of the structure-property relationship, and knowing how to control and manipulate atomic structure and defects to optimize materials' functionality. Computer simulations and theoretical modeling are carried out to aid the interpretation of experimental data. Fabrication of thin films with tailored microstructure and nano-assemblies to understand materials' electronic and magnetic response under applied stimulus is also incorporated.

Gaining a thorough understanding of the correlation between the structure and property of complex materials entails our adopting a wide range of characterization capabilities. One essential component of our program is developing advanced instruments and methods for high-resolution imaging, diffraction, and spectroscopy that can be broadly applied to quantitatively characterizing a spectrum of materials and their behaviors at the nanoscale. Such advancements require a significant resource suitable for a national laboratory setting, wherein applications to different model systems and strongly correlated oxides and energy-related materials can be demonstrated.

FY 2012 HIGHLIGHTS

The impact and progress of our program during FY 2012 includes, but is not limited to, unraveling switching behavior of various magnetic, ferroelectric, and multiferroic systems to understand nanoscale magnetism and ferroelectric, ferromagnetic, and ferroelastic coupling and the role of the magnetic degree of freedom in strongly correlated electron systems. We reveal what is the ultimate size limit of ferroelectric order in individual nanometer-scale crystals; how spatial distribution of the temperature dependent charge/orbital ordered nanoclusters attributes to the colossal magnetoresistance in manganites; how magnetic monopoles nucleation, propagation, and annihilation contribute to the magnetic ordering and reversal in frustrated spin-ice lattices; what is the origin of non-adiabatic spin torque and spin-dependent transport and current-driven magnetization dynamics in ferromagnetic materials and spintronic devices; why anion polarization can lead to superconductivity in Fe-based superconductors; what is the optimized microstructure of new electrode materials that can provide higher power and energy density, longer life, and safer lithium-ion batteries; and why imaging surface structure at atomic resolution is possible using low-energy secondary electrons.

Real Time TEM Imaging of Materials Transformations in Liquid and Gas Environments

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Funding:	$500,000

PROGRAM SCOPE

The objective 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 develop environmental cell TEM and result in better understandings of growth and chemical reactions of nanocrystals and mass transport induced structural changes in electrochemical processes important for energy applications.

FY 2012 HIGHLIGHTS

We have made significant progress on the study of shape control mechanisms during nanocrystal growth and the surfactant effects using liquid cell TEM. Our direct observation reveals, for the first time, growth pathways of platinum iron nanorods that small nanoparticles attach end-to-end into a crooked chain and then it straightens out to form a single-crystal rod. Studies further show details on how surfactants strongly affect nanoparticle shape evolution. This work helps to resolve the many years' debates on nanocrystal growth dynamics. This understanding of growth mechanisms contributes to rational design of materials with tailored properties.

During growth in liquids, nanoparticles are extremely dynamic with frequent changes in shape enabled by the ease of mass transport across the nanoparticle. Understanding the structural flexibility of nanoparticles during chemical reactions is critical since it strongly affects their function in applications, such as in heterogeneous catalysis. Using an environmental TEM, we have observed phase segregation of bimetallic PtCo nanocatalysts in different reactive gases studied. Migration of Co to the surface in an oxidation environment and inversion to Pt on the surface in a reducing environment were captured in real time. Our results show key details of oxidation pathways at the atomic scale. Combining these observations with modeling studies, we have identified the driving force for the phase segregation. In the next period, we will use liquid and gas environmental TEM to study the growth and transformation of Co-based nanocatalysts with different size and shape, including other functional materials systems. The success of these efforts will contribute significantly to the development of inexpensive, efficient energy-related technologies.

Soft Matter Electron Microscopy Program

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Funding:	$750,000

PROGRAM SCOPE

We will study charge transport in polymer membranes by electron scattering and microscopy. We focus on self-assembled nanostructures formed by bio-inspired peptoids and synthetic block copolymers within which ion transport is restricted to one of the nanostructures. We aim to determine the geometry and chain configurations that lead to the most efficient solid-phase ion-transporting channel. Spatially-resolved electron microscopy and energy-loss spectroscopy are crucial for obtaining the relationship between morphology and transport. Our microscopy techniques focus on maximizing spatial and energy resolution while minimizing radiation exposure and damage. We will manipulate and detect the incident, transmitted, and scattered electrons using aberration-correctors, high brightness instruments, and novel 3D image reconstruction algorithms. In-situ electron microscopy experiments to investigate the dynamic nature of soft materials on molecular and sub-molecular length scales have been designed. This project will investigate if the resolution in soft materials of interest can be extended to sub-nanometer length scales. We will develop materials with unique properties, e.g., membranes that become wetter when they are heated in air and mechanically robust solid electrolytes for battery applications.

FY 2012 HIGHLIGHTS

We have produced the first electron micrographs of proton-containing clusters in fuel cell membranes. An important barrier in the manufacturing of fuel cells is the lack of mobility of protons in the polymer membrane between the electrodes. We show that the protons are contained within clusters with an average diameter of 1.5 nanometers. Previous attempts to image these clusters were thwarted by the lack of contrast between the clusters and the surroundings and the "overlap" problem due to their small size. We have exploited the ability of the relatively heavy sulfur atoms to scatter electrons and obtained a dark field micrograph from a 35 nm thick film. The 1.5 nm clusters would overlap strongly in projection if they were uniformly distributed throughout the film. The key to success was the discovery of a processing methodology that resulted in the formation of ultrathin layers containing the clusters on the top and bottom surfaces of the specimen. Since protons must hop between clusters as they are transported in a fuel cell, the ability to independently determine the nature of clustering is crucial for designing the next generation of fuel cell membranes with improved proton mobilities.

Fundamental Mechanisms of Transient States in Materials Quantified by Dynamic Transmission Electron Microscopy (DTEM)

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Funding:	$1,002,000

PROGRAM SCOPE

We seek to study complex transient phenomena associated with rapid strongly driven processes in materials, such as the atomic level mechanisms and microstructural features for nucleation and growth associated with phase transformations in materials, specifically in crystallization reactions from the amorphous phase and martensite formation. We also will study the transient phase evolution in rapid solid-state reactions, such as those occurring in reactive multilayer foils (RMLF). The competition between nucleation rates and growths rates in these transformations determines the resultant structure and thus properties of the materials. These investigations are enabled by the unique in situ capabilities and the nanosecond time resolution of the dynamic transmission electron microscope (DTEM). This capability will allow us to develop a fundamental understanding of materials dynamics in systems where the required combination of spatial and temporal resolution are accessible by no other technique. In this regime, the DTEM is capable of studying complex transient phenomena with several orders of magnitude time resolution advantage over any existing in-situ TEM.

FY 2012 HIGHLIGHTS

We have imaged the evolution of rapid solidification in Al and Al-Cu alloys, transient microstructures in RMLF, and rapid crystallization of phase change materials, binary intermetallic glasses, and single component amorphous Ge. In the Ni-Al and Ti-B RMLF studies, we have identified the important role that a transient liquid phase plays in heat flow and temperature evolution that affects structure development. We have identified and quantified C-curve behavior in the crystallization of amorphous NiAl and GeTe. We have also found no identifiable C-curve behavior in the crystallization of amorphous Ge within the time resolution of the DTEM. We have also found that rapid solidification of pure Al in nanoscale films is dominated by heat flow, thus leading to smooth solidification fronts at the level of the grain scale, but the addition of Cu slows the solidification markedly and causes growth front morphological instability. We have tracked the crystallization velocity of GeTe phase change material in situ and accurately measured the high temperature crystallization rate for the first time in this important class of electronic materials.

We have commissioned the movie mode capability on the DTEM, thereby allowing the capture of a sequence of images from a single irreversible event occurring in situ in the specimen. We acquired nine images that make a short movie of the event. We have used movie mode to study the microstructural evolution at the propagating reaction front in RMLF. We have tracked the position of the interface in a transforming solid as a function of time and observed the nature and mechanisms involved with the interaction of the interface with microstructural features that allow us to more effectively model phase transformation kinetics.

Probing Coupled Metal-Insulator and Ferroic Transitions from the Atomistic to Mesoscopic Scales

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Funding:	$600,000

PROGRAM SCOPE

The coupling between electronic and ferroic behaviors is one of the most intriguing aspects of condensed matter physics, with examples ranging from phase separation in complex oxides, metal-insulator transitions in ferroelastic oxides, and complex electronic ordering patterns in superconducting and charge-density wave materials. The overarching goal of this project is to reveal the mechanisms of coupled electronic (metal-insulator) and ferroic (ferroelastic and ferroelectric) transitions from atomistic to mesoscopic scales by exploring coupled electronic and atomistic structures on the length-scale of a single domain, structural defect, and domain wall. The program will develop and exploit the synergy between advanced scanning probe microscopy that offers the capability to explore and actively manipulate local order parameters in nanoscale volumes, artificial-intelligence and multivariate methods for theory-experiment matching, and established methodologies of surface science and oxide growth. Unraveling and subsequently understanding the energy balance between competing interactions will pave the way to deterministic design of novel electronic materials and 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 2012 HIGHLIGHTS

Research effort in FY 2012 was centered on the dual goal of understanding the coupling between order parameters at the topological defects in ferroic materials, including domain walls and ferroelectric vortex cores, and the role of mobile ionic defects on these behaviors. On the mesoscopic level, we explored experimental signatures of the bias- and strain-induced vacancy dynamics in simple oxides, including NiO, through the high-dimensional scanning probe microscopy measurements, and developed an associated Ginzburg-Landau based theoretical description. On the atomistic level, we extended the applicability of local crystallographic mapping to scanning tunneling microscopy data, allowing for mapping surface electrochemistry and order parameter fields on the atomic level in manganites and high-temperature superconductors. This project led to the development of experimental pathways to explore the coupling between chemical and physical behaviors on the atomic level.

Probing Phase Transitions, Chemical Reactions, and Energy Transfer at the Atomic Scale: Multifunctional Imaging with Combined Electron and Scanning Probe Microscopy

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Funding:	$744,000

PROGRAM SCOPE

Electrical bias-induced phase transitions and electrochemical reactions underpin a wide range of phenomena—from global issues such as energy generation, storage, and conversion to the fundamental science of order parameter-structure couplings. The overarching goal of this proposal is 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 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 phenomena. These will be achieved by the synergistic pursuit of the following aims: (1) studies of irreversible electrochemical processes including oxygen vacancy injection, vacancy ordering, and the formation of crystallographic shear defects; (2) studies of hysteretic processes including electrostatically-driven structural changes and phase transitions in ferroelectrics and at ferroelectric interfaces; and ultimately, (3) studies of 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, at the single-atom and single electron level, and link these to atomistic and mesoscopic models. This will enable optimization of a broad range of energy and information technologies—from fuel cells, supercapacitors, and batteries to memristive data storage and logic devices.

FY 2012 HIGHLIGHTS

Research efforts in FY 2012 have led to significant advances in characterization and understanding of vacancy ordering phenomena in cobaltites. An approach based on the extrapolation of chemical expansivity concept down to one unit cell level was shown to provide precise quantitative measurement of local vacancy concentration. A Ginsburg-Landau based theoretical description of vacancy ordering was developed; quantitative parameters of this description, including gradient terms, were demonstrated to be recoverable from local studies of defects in vacancy ordered systems. Oxygen vacancy behavior was also investigated in situ in amorphous TiO_2-based memristor device stacks, where we have shown that crystallization due to Joule heating by leakage current precedes oxygen redistribution, leading to the formation of the seeds of conductive filaments consisting of Magneli phases. Finally, continuing our studies of order parameter coupling, we were able to show how changing interface termination in bismuth ferrite thin films leads to formation of a new interface phase with different polar order, with the change being driven by octahedral tilt interactions at the interface.

Scanning Transmission Electron Microscopy: Atomic Structure and Properties of Materials

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Funding:	$2,588,000

PROGRAM SCOPE

In recent years, the successful correction of aberrations in the electron microscope has provided sub-Ångstrom resolution for imaging, combined with unprecedented sensitivity for spectroscopy. For the first time, atomic resolution can be achieved with accelerating voltages as low as 60 kV—avoiding most damage events in materials such as graphene—and two-dimensional spectroscopic images of composition and electronic structure have become feasible. Several of the most exciting areas of current condensed matter and materials physics can best, perhaps only, be understood with a real-space probe of atomic dimensions. We propose to focus on three such areas: defect configurations in graphene, complex oxide heterostructures, and nanostructures for solar and lighting applications. In all cases, the complexity of the system means that a real space probe is critical to elucidate the local atomic and electronic structure and the link with the macroscopic properties that are of interest for potential applications. We will also explore the limits to image resolution and sensitivity in this new sub-Ångstrom regime, and investigate new imaging modes capable of providing nanoscale maps of optical and electronic properties.

FY 2012 HIGHLIGHTS

Aberration-corrected scanning transmission electron microscopy has been used to study a number of topical areas in energy related materials. In graphene, point defects have been investigated at the single atom level; their atomic structure, chemical bonding, and even their dynamics have been followed through gentle excitation by the electron beam. A localized plasmon enhancement has been observed at a single silicon point defect, suggesting new directions in optoelectronic communications. In carbon nanotube-graphene systems, we found that iron-nitrogen impurity complexes are efficient oxygen reduction electrocatalysts for next generation fuel cells, a potential replacement for costly platinum. In oxide materials, a combination of picometer precision atomic displacement mapping and electron energy loss measurements of charge transfer have resolved the controversy over the origin of the electrical conductivity at the interface of the two insulators: lanthanum aluminate and strontium titanate. Magnetism in oxide nanoparticles has been mapped at the nanoscale using electron magnetic chiral dichroism, revealing that capping the nanoparticles with an organic acid restores magnetism in the normally dead surface layer, a beneficial effect for potential applications. The origin of white light emission in sub-2-nm CdSe nanoclusters has been deduced through a combination of atomic resolution imaging and first-principles quantum molecular dynamics. Below a critical size, the nanoclusters take on a dynamic disordered structure when excited. This fluxionality leads to rapidly varying electronic structure, leading to emission over a range of wavelengths, i.e., white light emission. This result has significant implications for future white light emitting materials.

Structure-Property Relationship of Disordered Nanoporous Carbons

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Funding:	$567,000

PROGRAM SCOPE

The goal of this project is to understand the impact of local atomic order and topological defects of disordered nanoporous carbons and related materials on specific properties associated with the presence of a large fraction of carbon atoms exposed at internal surfaces. To achieve this goal, we will focus on two specific aims: (1) understanding the relationship between local atomic structure and the large scale architecture of nanoporous carbon, and the impact on physical properties; and (2) understanding how local structures determine adsorption interactions and the behavior of trapped molecular species confined in porosity. Our approach will combine synthesis, advanced characterization, simulation, and modeling. We will utilize state-of-the art neutron and x-ray scattering facilities at HFIR, SNS, and APS; high speed computational facilities at ORNL and other DOE facilities; and the high-resolution microscopy facilities at ORNL.

We will utilize the above knowledge to establish guidelines to design and build materials tailored for energy storage and conversion; and to develop new techniques, methods, and procedures applicable to other porous materials of comparable properties or to other applications operating on corresponding principles. This proposal pertains to the grand challenges faced by materials science today: *How can we design new and revolutionary materials with tailored properties for more energy efficient solutions? How can we create and control those remarkable properties of materials that emerge from complex* *correlations of atomic and electronic constituents? How does matter behave and how can we control it at conditions far from equilibrium?*

FY 2012 HIGHLIGHTS

Results from atomic resolution electron microscopy and molecular dynamics simulation showed that nanoporous carbons are comprised of wrinkled, defective sheets of graphene, arising from the presence of large domains of correlated 5- and 7- fold defects that buckles the sheets, creating porosity. These non-hexagonal defects in graphene sheets give rise to sheet corrugation, affecting the stacking of graphitic layers and determining macroscopic properties such as surface area, pore volume distribution, gas adsorption capacity, and molecular sieving selectivity. Understanding the origin of the porosity will make it possible to tailor future properties through selective processing and doping.

We used adsorption models to calculate pore-size dependent hydrogen adsorption in realistic nanoporous carbon structures. We also demonstrated that an *ab initio* treatment of physisorption leads to different optimal pore sizes for adsorption. We are presently extending this to methane and other gasses.

Finally, we have completed construction and tested the the first-of-kind high pressure cryo-cell for in-situ small angle neutron scattering experiments. This cell will allow us to study the phase behavior of adsorbed hydrogen as a function of pressure and nm-scale pore size at cryogenic temperatures.

Correlated Materials - Synthesis and Physical Properties

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Funding:	$1,682,000

PROGRAM SCOPE

The overarching goal of our research is to understand, and ultimately control, emergent behavior in strongly correlated quantum materials. This broad class of materials holds promise for future applications directly relevant to energy security, affecting technologies from energy distribution to improved power electronics, to more efficient computing. There are, however, many deep intellectual questions that need to be addressed in order to realize this potential. There are also many opportunities for the development of novel materials with improved properties. The intellectual focus of this FWP sits at the intersection of these challenges and opportunities. Big questions that we collectively address include *What are the rules and organizing principles governing emergent behavior in quantum materials? What is the nature of the coexisting and competing phases in high temperature superconductors, and how do they determine/limit the maximum critical temperature? What ordered states arise in oxide systems with strong spin-orbit coupling, both in bulk materials and at interfaces?* And finally, *How does quenched disorder affect quantum criticality and inhomogeneous electronic states* *in strongly correlated materials?* Our research addresses these challenging questions in the context of a range of complex quantum materials.

FY 2012 HIGHLIGHTS

Time reversal symmetry breaking in La2-xBaxCuO4 (arXiv:1203.2977) – Recent experiments in the original cuprate high temperature superconductor, La2-xBaxCuO4 (LBCO), have revealed a remarkable sequence of transitions with polar Kerr effect using a Sagnac interferometer, which is sensitive to timereversal-symmetry breaking (TRSB). Hysteretic behavior of the Kerr signal suggests that TRSB occurs well above room temperature, an effect that was previously observed in high quality YBCO crystals.

Divergent nematic susceptibility in an Fe-arsenide superconductor (arXiv:1203.3239) – We have developed a new methodology using uniaxial strain which can probe the “nematic” response of materials. Our measurements of the prototypical system Ba(Fe1−xCox)2As2 show that the structural phase transition is fundamentally driven by an instability in the electronic part of the free energy, and reveal an electronic nematic quantum phase transition at the composition with optimal doping.

Phases of the infinite U Hubbard model on square lattices (Phys. Rev. Lett. 108, 126406 (2012)) – We carried out extensive DMRG calculations on long ladder systems of width between 2 and 6 sites in the extreme large U limit. For a range of doped hole concentrations $0 < x \leq 0.25$, we find a half-metallic ferromagnetic, and charge and spin-density wave insulating phase, and regions of 2-phase coexistence, but no superconducting phases. This result implies that unconventional superconductivity is not a generic feature of the Hubbard model in the strong coupling limit, confirming that high temperature superconductivity is intrinsically an intermediate coupling effect.

Critical thickness for ferromagnetism in LaAlO3/SrTiO3 heterostructures (arXiv:1201.1063) – We imaged the magnetic landscape in a series of LAO/STO samples of varying LAO thickness and found that ferromagnetic patches appear only above a critical thickness, similar to the critical thickness for conductivity. Consequently we conclude that an interface reconstruction is necessary for the formation of magnetism.

Experimental Condensed Matter Physics

Institutions Receiving Grants

Probing the Origins of Conductivity Transitions in Correlated Solids: Experimental Studies of Electronic Structure in Vanadium Oxides

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Funding:	$150,000

PROGRAM SCOPE

The scientific and technological interest in solid state conductivity transitions is enormous. These transitions can be driven by many external and internal mechanisms. Vanadium oxides display particularly complex and fascinating transitions, and are prototypical correlated materials, allowing important physical themes to be explored both experimentally and theoretically.

This program aims at the spectroscopic measurement of the electronic properties of a selection of vanadium oxides. The primary goal is to use the knowledge to be gained on the electronic structure of the 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 (XES), soft x-ray absorption spectroscopy (XAS), and photoemission spectroscopy (PES).

FY 2012 HIGHLIGHTS

(1) Strain dependence of bonding and hybridization across the metal-to-insulator transition in VO_2: VO_2 provides a textbook example of a metal-to-insulator transition (MIT) with its large (~ 10^4) discontinuity in the conductivity and the rich tunability of its properties with alloying or strain. However, the nature of the transition itself still remains a challenge to explain, either driven by the lattice or by electron correlation effects. VO_2 has a rutile structure in the insulating phase, but a monoclinic structure in the metallic phase. This structural transition imposes a significant bottleneck on the timescale of the conductivity transition. We used XES and XAS to show that the MIT of moderately strained VO_2 thin films still involves the lattice even though the transition temperature has been lowered, and we found that the role of the O ion has a surprising dependence on the strain. Such strong strain-dependent changes in the hybridization between V and O states are not expected from band theory, and point towards a more significant role for the O ion than previously considered.

(2) Crossover from Peierls-like to Mott-like transition in highly strained VO_2: We observed a crossover from a Peierls-like transition to a Mott-like transition with an increase in tensive strain along the c_R-axis in VO_2. XAS and XES demonstrated the absence of the large structural distortion at the MIT that characterize bulk and moderately strained VO_2. PES measurements revealed a weak insulating gap as well as the suppression of orbital redistribution across the transition. Our observations have important implications for novel functional material engineering of VO_2, suggesting a route towards circumventing the structural bottleneck in the ultrafast timescale of the MIT.

Quantum Electronic Matter in Two Dimensions

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Funding:	$175,000

PROGRAM SCOPE

We seek to answer fundamental questions about large collections of Nature's simplest elementary particle, the electron. These electrons are confined to two dimensions, both in semiconductor quantum wells and in single and few layer graphenes. Electrons so confined are hardly a scientific curiosity. Essentially all modern consumer electronics is based upon transistors containing two-dimensional (2D) electron systems, and there is already a vast amount of current research aimed at harnessing the potential of graphene for technological purposes.

For example, we are presently completing the construction of a new apparatus that will allow us to cool 2D electron systems to roughly 0.001 degree Kelvin above absolute zero. With this advanced capability, we will be able to search for new, extremely fragile, collective electronic states. This is an essential step for the field since the quality of the samples now being grown is so high that present refrigeration methods are inadequate for their complete study. We are confident that Nature will reward those making this step.

Graphene represents another focus of our research. We have recently expanded our graphene research goals to include exploring the influence of small numbers of heavy adatoms (e.g., Os) deposited on the graphene surface. Recent theoretical work has predicted that such adatoms will "lend" their strong spin-orbit coupling to the Dirac electrons in the graphene. This is expected to convert graphene into a genuine 2D topological insulator (i.e., a system which is insulating in its interior but conducting at its boundary).

FY 2012 HIGHLIGHTS

(1) We completed a careful study of transport in ABA-stacked trilayer graphene. Major conclusion: Three is the smallest number of graphene layers that is needed to establish a true semi-metallic state (as in the infinite layer system, graphite).

(2) We completed the most careful study to date of the thermopower of 2D electron systems in the regime of the fractional quantum Hall effect. Major findings: (a) Essentially all known fractional quantum Hall states in the first excited Landau level have now been cleanly observed in thermoelectric transport. (b) We were the first to observe the near-discontinous collapse of the thermopower of the so-called re-entrant integer at very low temperatures (~40 mK). This collapse is a strong indicator of a first-order phase transition into these insulating electronic states. (c) Our measurements of the thermopower near the 5/2 fractional quantized Hall effect are in rough quantitative accord with recent theories based on non-abelian quasi-particle statistics.

RECOVERY ACT - Control Graphene Electronic Structure for Energy Technology

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Funding:	$0.00 (Research was supported with prior fiscal year funding.)

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 of approaches and exploit the unique graphene properties for innovative energy technology.

FY 2012 HIGHLIGHTS

(1) Achieve Screening-Engineered Field Effect Solar Cells: Photovoltaics (PV) are a promising source of clean renewable energy, but current technologies face a cost-to-efficiency trade-off that has slowed widespread implementation. We have developed a new PV architecture, screening-engineered field-effect photovoltaics (SFPV), that in principle enables fabrication of low-cost, high-efficiency PV from virtually any semiconductor, including the promising but hard-to-dope metal oxides, sulfides, and phosphides. Prototype SFPV devices have been constructed using nanometallic electrodes and graphene electrodes. The prototype devices operate successfully in accord with model predictions.

(2) Achieve Electrical Control of Optical Plasmon Resonance with Graphene: We achieved the first experimental demonstration of a plasmonic device integrated with graphene where the plasmon resonances can be controlled via electrostatic gating of graphene. For the demonstration, we deposit graphene on top of a single gold nanorod on the glass substrate, which has strong localized surface plasmon resonance at 870 meV. Also, we fabricate top-gate on graphene with ionic liquid as gating medium to achieve high doping efficiency. A light scattering experiment shows that the plasmon resonance can be shifted by 20 meV and resonance scattering intensity can be varied by 30 percent. Our study indicates that electrostatically-doped graphene can provide great flexibility to the potential application for plasmonic devices and metamaterials given graphene’s excellent compatibility to different processing and micro/nanofabrication methods.

Investigating the Role of Ferromagnetic Materials on the Casimir Force

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Funding:	$150,000

PROGRAM SCOPE

The Casimir effect predicts a force between macroscopic bodies that are electrically neutral. The force results from the spectral modification of the zero-point oscillations of the electromagnetic field due to the presence of the macroscopic objects. Here we propose to experimentally investigate the role of ferromagnetic materials in the Casimir force. Contrary to previous thought, it is now realized that soft ferromagnetic materials will have large effects on the Casimir force through their impact on the zero frequency term. The Casimir force for ferromagnetic materials is also found to be strongly dependent on the inclusion or neglect of the electron-phonon scattering (Debye relaxation) in the treatment of the material properties. Thus the measurement of the Casimir force with ferromagnetic materials might be the most sensitive to understanding the role of scattering processes due to zero-point photons. Additionally, initial calculations predict that the Casimir force between a ferromagnetic dielectric and a normal metal can even be repulsive at some separation distances if the electron scattering is neglected. Thus these experiments will clarify the proper treatment of the electron relaxation losses in the Lifshitz theory of the Casimir force. In general, the field is gaining widespread scientific attention due to its importance in fundamental science as well as applications. The Casimir effect is significant in micromachines when electrode surfaces approach sub micron length scales, at which point the value of the Casimir force is of the same order as the electrostatic force that is presently used for actuation.

FY 2012 HIGHLIGHTS

The accomplishments to date made possible by the award are 15 refereed publications in journals such as *Physical Review Letters*, *Physical Review A*, *Physical Review B*, *Applied Physics Letters*, and *International Journal of Modern Physics A* and *B*. In addition, we presented two plenary conference talks, two regular conference talks, one colloquium, and eight APS talks.

In this period, after the completion of the building of high precision force measurement setup based on detecting frequency shift, we tested it on measuring the Casimir force between an Au sphere and Au plate. After this, we started measurements of the Casimir force between a ferromagnetic Ni plate and an Au sphere. The latest submitted publication to *Physical Review Letters* reports the first demonstration of the Casimir force between two ferromagnetic boundary surfaces. The experimental data were found to be in excellent agreement with the predictions of the Lifshitz theory for magnetic boundary surfaces combined with the plasma model approach to description of low frequency permittivity of the metal. Of particular importance is that for two magnetic surfaces, an additional role due to patch potentials will lead to a decrease of the measured force, which is opposite to that required to reconcile the data with the Drude model description.

Cold Exciton Gases in Semiconductor Heterostructures

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Funding: $150,000

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 will be to explore these properties of indirect excitons to study cold excitons in lattices and to study spin-related phenomena in cold exciton gases.

We will study exciton transport and coherence in lattices as a function of the lattice amplitude and structure as well as the exciton number per lattice site and temperature. We will also develop stirring potentials for excitons based on the recently developed moving lattices for excitons. We will probe if the stirring potential creates vortices of cold excitons and study the dependence of the vortex pattern on the amplitude and angular velocity of the stirring potential. 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 2012 HIGHLIGHTS

We observed patterns of spontaneous coherence in a cold gas of indirect excitons. We observed spontaneous coherence and condensation of indirect excitons in an electrostatic trap. We developed two-dimensional electrostatic lattices for indirect excitons; the lattice structure is set by the electrode pattern, the amplitude of the lattice potential is controlled by voltage, and the number of excitons per lattice site is controlled by laser excitation. We observed spin textures in a coherent gas of indirect excitons.

Electromagnetic Response of Correlated Electron Systems

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PROGRAM SCOPE

The physics of correlated electron systems is rich, and many phenomena discovered in these materials still elude a thorough understanding. The complexity of these solids is, at least in part, related to their tendency towards the formation of electronic and/or magnetic inhomogeneities at diverse length scales. These effects have been systematically documented with the help of x-ray and neutron scattering, various scanning probe techniques, and other methods. Nevertheless, the dynamical properties of individual electronic phases commonly coexisting in correlated electron matter on the nano-meter (nm) scale remain largely unexplored because methods appropriate to the study of charge dynamics (transport, infrared/optical, and many other spectroscopies) lack the required spatial resolution. This deficiency is fundamental and ought to be remedied in order to make critically needed advances in our understanding of complex correlations phenomena. The challenges involved in elucidating the physics of correlated systems call for the development of novel experimental approaches. The proposed program features new methods, including nano-scale infrared (IR) imaging/spectroscopy and x-ray nano-imaging, which in combination will allow the PI to significantly advance the present experimental understanding of correlated electrons.

The proposed program will focus on two systems: nickelates and graphene. Both classes of materials feature a wealth of new physical phenomena which are yet to be understood. Both classes of materials also hold great promise for technological applications. Therefore, the proposed program will allow the PI to explore and exploit the complex and novel many-body effects arising in these systems. The goal of the proposed IR nanoscopy studies is the systematic investigation of the role of electronic phase separation in the insulator-to-metal transition regime of nickelates. Specifically, near-field IR experiments will be performed for a series of ultrathin films of $NdNiO_3$ and superlattices based on $LaNiO_3$. The electronic properties of these compounds can be controlled through strain and epitaxy. These nanoscopy measurements will be augmented by nano-scale structural characterization using facilities at the Advanced Photon Source and by in-house broad-band ellipsometric measurements. The proposed work on nickelates will provide the most complete experimental picture to date of the emergence of the metallic state in this prototypical family of correlated oxides. The second component of the program will focus on the methodical examination of the electronic and plasmonic response of graphene using in-house nanoscopy instrumentation as well is IR microscopy facilities at the Advanced Light Source. The role of electronic correlations and many-body effects in graphene is an important unresolved problem. The PI will investigate a new generation of graphene samples, including specimens on BN substrates and also free-standing, suspended graphene. This work will help to ascertain how disorder and many-body effects affect the intrinsic properties of graphene.

Nanostructured Materials: From Superlattices to Quantum Dots

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PROGRAM SCOPE

This project is dedicated to the main issues that arise when materials are nanostructured in one, two, and three dimensions. This comprehensive project includes preparation of nanostructures using thin film and lithography techniques; characterization using surface analytical, scanning probe microscopy, scattering, and microscopy techniques; and measurement of physical properties. The important physical properties to be investigated include confinement, a variety of proximity effects in 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. This has lead to and will possibly produce and/or uncover unique new physical phenomena and devices. In particular, this research has major impact in the area of nanomagnetism, a major forefront research area world-wide.

Specific physical problems to be investigated include important basic research issues in exchange bias in magnetic bilayers; confinement of magnetism by geometric boundaries; proximity effects between ferromagnets/antiferromagnets, metals/oxides, organics/metals; and their behavior at ultrafast times. Moreover, some of the techniques (especially structural characterization) developed under this project are supplied free of charge to other researchers in a wide variety of related areas. This research has direct impact on DOE's Five Challenges for Science and Imagination and will develop the basic research foundation of many technologies important for the nation.

FY 2012 HIGHLIGHTS

We have performed several experiments directly related to the aims of this project. In the field of Exchange Bias, we performed two experiments that help us identify the origin of the phenomenon. By preparing hybrid ferromagnetic/antiferromagnetic samples with nanostructured antidots prepared by Focused Ion Beams (FIB), we uncovered the effect of bulk uncompensated pinned spins on Exchange Bias. Through a detailed structural and magnetic study, we have been able for the first time to observe the connection between exchange bias and the so called "Verwey transition" in Fe3O4. We have performed a detailed study of the ferromagnetism of one-dimensional chains in organic metallo-phthalocyanine films, which addresses one of the fundamental issues related to the effect of dimensionality and magnetism. In a tour-de-force experiment, in collaboration with scientists at the Los Alamos National Labs, we have shown the absence of ferromagnetism at the interfaces of $LaAlO_3/SrTiO_3$. This is a major development since all measurements to date claiming spectacular effects at this interface were based on bulk magnetic measurements and only neutron scattering could ascertain unequivocally the origin of the fleeting magnetic signals encountered.

Superconductivity and Magnetism in d- and f-Electron Materials

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Funding:	$300,000

PROGRAM SCOPE

The primary emphasis of this project 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 focus on the growth of high quality single crystal specimens. Materials investigated include Fe-pnictide high temperature superconductors, unconventional U-based superconductors, magnetically ordered rare-earth compounds, and heavy fermion f-electron materials. The anisotropic normal and superconducting state properties of these materials are studied as a function of concentration of chemical constituents, oxygen vacancy concentration, 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. Physical properties of high-T_c superconductors and thermoelectric materials that are important for their performance in technological applications have been characterized. Of particular interest are phenomena associated with the interplay between superconductivity and other types of spin and charge order.

FY 2012 HIGHLIGHTS

Much of our recent research falls into seven principal categories: correlated electron behavior in the noncentrosymmetric $Ln_2T_{12}P_7$ compounds, Fe-pnictide based superconductors, valence fluctuations in $Ce_{1-x}Yb_xCoIn_5$, superconductivity and magnetism in LnT_4X_{12} filled skutterudites, high temperature superconductivity in the cuprates, the interplay between weak ferromagnetism and superconductivity in UCoGe based materials, and hidden order, magnetism, and superconductivity in URu_2Si_2. A few highlights are mentioned below.

The temperature (T) - magnetic field (H) phase diagram for single crystals of the noncentro-symmetric compound $Yb_2Fe_{12}P_7$, with a curious crossover from a magnetically ordered non-Fermi-liquid (NFL) phase at low H to another NFL phase at higher H, was established. An infrared and optical study of a single crystal of the superconductor LaFePO, carried out in collaboration with D. Basov's research group, yielded clear evidence of electronic correlations in metallic LaFePO, suggesting that electronic many-body effects are important in iron pnictide superconductors, despite the absence of a Mott transition.

An investigation of the system $Ce_{1-x}Yb_xCoIn_5$ ($0 \le x \le 1$) reveals that many of the characteristic features of the x = 0 correlated electron state are stable for $0 \le x \le 0.8$, apparently due to cooperative behavior of the Ce and Yb ions, involving their unstable valences. Recent spectroscopic studies indicate Ce and Yb valences of ~3+ and ~2.3+, respectively, supporting this interpretation. The linear decrease of T_c with x towards 0 K as x approaches 1 is in marked contrast to other heavy fermion superconductors where T_c scales with the coherence temperature. A study of the system $URu_{2-x}Fe_xSi_2$ revealed a surprising two-fold enhancement of the “hidden order”/large moment antiferromagnetic phase boundary, which may provide clues to the identity of the mysterious “hidden order” phase.

Coherent Excitations in Disordered Quantum Materials

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Funding:	\$0.00 (Research was supported with prior fiscal year funding.)

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 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.

FY 2012 HIGHLIGHTS

Quantum Antiferromagnetism: The dipolar force between magnetic moments is present in all magnetic systems, from classical to quantum magnets and from bulk materials to nanoparticles. However, while critical phenomena are well studied in systems with short range forces, dipolar-coupled systems, especially antiferromagnetic ones, have received less scrutiny, mainly due to a dearth of physical realizations. We have undertaken a full suite of neutron scattering, specific heat, and magnetic susceptibility studies of $LiErF_4$, establishing it as a model dipolar-coupled antiferromagnet with a quantum phase transition in applied field $H_c = 4.0 \pm 0.1$ kOe. The intrinsic frustrated nature of the dipolar interaction appears to lead to an effective reduction in the dimensionality of the system, with implications for the study of magnetic thin films and nanomagnetic storage media and promise for testing longstanding theoretical predictions.

Two-Dimensional Quantum Magnetism: The transition from the fundamental quantum mechanics of two spin ½ objects to the complex physics of an interacting spin lattice touches on a good portion of modern condensed matter physics. The Shastry-Sutherland 2D interacting dimer model has played an influential role in developing the field because it is sufficiently simple to be exactly soluble, but sufficiently rich to capture interesting physics. We have mapped out the development from isolated dimers to long-range magnetic order via a high-pressure, high-resolution x-ray synchrotron study of the physical realization of the Shastry-Sutherland model, $SrCu_2(BO_3)_2$. Using a diamond anvil cell cooled down to cryogenic temperatures, we are able to track explicitly the suppression of the singlet-triplet gap at a second-order quantum phase transition, followed at higher pressure (~4.5 GPa) by a first-order structural/magnetic transition.

Transport and Magnetotransport in Colloidal Quantum Dot Films

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Funding:	$0.00 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

This project investigates experimentally the electronic transport through self-assembled films of colloidal quantum dots (CQDs). The quantum dots are of order 10 nm in diameter or smaller, made by colloidal chemical synthesis. These are materials typically explored for roll to roll solar cells, low-cost photodetectors, and light emission devices. These applications may be limited by the electronic transport through the arrays; this motivates the basic studies of the project.

Rather monodispersed dots are used to eliminate one source of disorder and to start with systems where the energy levels are well separated and understood within the individual quantum dots. In parallel with chemical methods devised to improve the electronic transport parameters such as mobility, a key originality of the project is the control of the charge density in the dots. In addition, the project explores the effects of temperature, bias, and magnetic field. Models developed for transport in disordered conductors are applied to the arrays of quantum dots. Incoherent hopping, rather than band-like conduction, is typically observed. The monodispersed quantum dot assemblies allow for a quantitative application of these models at different state density, tunable by the Fermi level, and temperature. Controlling the magnetic properties through the charge density and the doping of magnetic impurity is the other aspect of the project.

FY 2012 HIGHLIGHTS

HgTe provides a new class of narrow gap CQD, which are also interesting for their potential as mid-infrared materials. An electrochemical study showed that multilayer films of HgTe CQDs can be stably charged n- and p-type with several carriers per dots, and this was confirmed by infrared spectroscopy. Similar mobilities, up to 0.1 cm^2/Vs, were observed for both carriers. However, the p-type films show larger photocurrent while the n-type films show larger magnetoresistance. The 1/f noise in the conductivity was studied as a function of the carrier numbers, uncovering very large Hooge constants for this system [J. Phys. Chem. C 116, 1344-1349 (2012)].

In quantum dot solids, a redshift of the absorption is often interpreted as arising from electronic coupling between the quantum dots. We performed a thermal deflection spectroscopy study of colloidal CdSe quantum films, treated with ammonium sulfide and annealed, and observed very large spectral redshifts and Urbach tails that extend below the bulk bandgap even for room temperature processing. However, CdSe/ZnS and CdSe/CdS quantum dot films did not show such effect. It was therefore concluded that, at least for the frequently studied CdSe system, electronic coupling between dots cannot account for the absorption tails and is unlikely to account for most of the redshift. The absorption tails and redshifts were attributed to surface states [J. Chem. Phys. 137, 154704 (2012)].

High-Bandwidth Scanning Hall Probe Imaging of Driven Vortices in Periodic Potentials

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Funding: $149,000

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 standard transport and magnetization measurements, to be uncovered.

Recent lithographic advances have made it possible to fabricate superconducting films that present a variety of periodic potentials to vortices in the film. Interesting effects of commensurability arise when the vortex spacing matches the period of the underlying potential, including strong increases in the critical current and dips in the resistance, indicating that vortices become particularly strongly pinned at these special matching fields. More recently, attention has turned to the dynamics of vortices driven across the film by the imposition of an external current. Again, commensurability has a profound effect on the depinning of vortices from their static configurations, and on the detailed nature of their dynamical trajectories.

In order to understand the nature of these dynamical states, this project will employ high-bandwidth scanning Hall probe microscopy to image the trajectories of vortices moving in a periodic potential. The technique uses a powerful combination of standard low-bandwidth imaging with several high bandwidth imaging modes, including a method of making high-speed movies for vortices driven by an ac current in a periodic potential. Using these advanced imaging techniques, many of the outstanding questions concerning vortex dynamics in these systems can be directly addressed.

FY 2012 HIGHLIGHTS

This project was funded with a start date of August 1, 2012, so the project was underway for only two months during Fiscal Year 2012. During this time, we have begun work on the three critical tasks required for this project. First, we have adapted our existing thermal evaporation system for fabricating the superconducting films to be used in the project. Second, we have made progress on using electron-beam lithography to define submicron Hall sensors and to fabricate the patterned substrates on which the films will be grown. And last, we have begun adapting our current closed-cycle cryocooler to work at the lower, more stable temperatures required for studying superconductors, and have designed the vibration-isolation stage needed for the scanning Hall probe microscope to reach its ultimate resolution.

Spin Wave Interactions in Metallic Ferromagnets

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Funding:	$162,000

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 and phonons, will be used to explore the fundamental nature of these effects.

FY 2012 HIGHLIGHTS

Highlights from FY 2012 include measurements of propagating spin waves in yttrium iron garnet, a material that provides an ideal combination of high magneto-optical response and low damping that often serves as a model system for spin dynamics investigations. Space- and time-resolved Brillouin light scattering measurements were carried out to explore the time evolution of the nonlinear parametric pumping process, which involves the conversion of spin waves or magnons into two magnons with frequencies of half that of the pumping frequency through a process known as three magnon splitting. This is a useful technique to generate higher k-vector magnons in a controlled manner, and these measurements will provide insight into the temporal aspects of the three magnon splitting as well as the confluence process that involves the subsequent recombination of the parametrically pumped magnons in the backward volume wave configuration. We have also designed and constructed a stage for heating magnetic samples to investigate thermal effects on spin wave processes.

Dynamics of Electronic Interactions in Superconductors and Related Materials

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Funding:	$220,000

PROGRAM SCOPE

The goal of this project is to utilize high-resolution angle-resolved photoemission (ARPES) to measure and understand the underlying electronic structure and electronic interactions in cuprate high temperature superconductors and related compounds. While ARPES has arguably been among the most successful of all probes in lending information about the electronic interaction in cuprates, progress has still been greatly hindered because we had a lack of quantitative methods to analyze and understand the data. This has changed with the introduction of new analysis techniques and new theory by us (see highlights), and we have been and will continue applying these new methods and ideas to a very wide range of doping values, sample temperatures, and momenta. We will utilize our unique laser-based ARPES instrument in Boulder as well as excellent access to synchrotron instrumentation.

FY 2012 HIGHLIGHTS

Two major advances have significantly altered the landscape for both the superconducting and strange metal phases. The first is the new TDoS (Tomographic Density of States) method that we introduced, 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, we find that the pair-breaking Γ is large and strongly temperature-dependent, and appears to play a critical role in cuprates. The TDoS method is ideally and uniquely suited for uncovering these details. We have completed some studies along these lines and are continuing in earnest to fully take advantage of the new opportunities to uncover the new physics. The second major advance is our new ARPES-driven phenomenological understanding of the strange metal state across all dopings, energies, and temperatures. All tests so far indicate the robustness of this new phenomenology, including direct extensions to transport, optics, thermodynamics, etc.

Transport Studies of Quantum Magnetism: Physics and Methods

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PROGRAM SCOPE

In this project, we carry out experimental studies of quantum spin systems using the electrical and thermal transport measurements, aiming to understand the novel state ground states with unique properties. Thermal and electrical transport measurements are well-suited for this goal since it directly probes the low-energy excitations and their propagation and interactions. We are also developing the novel thermometry particularly tailored for the thermal transport measurement. We utilize the shot noise of lithographically defined tunnel junctions to determine the temperature in a primary sense, i.e., not requiring any form of calibration, over a wide temperature range. This technique will overcome several nuisances and limitations of currently available thermal conductivity measurements and allow us to perform more convenient and accurate measurements under the extreme conditions such as high magnetic field.

FY 2012 HIGHLIGHTS

We have heavily focused on investigating the unusual chiral Hall effect in Fe doped MnSi ($Mn_{1-x}Fe_xSi$) as well as MnSi under high pressure. In the pure MnSi, great enhancement of the chiral signal in the larger temperature range was observed, as the critical temperature (T_C) decreases as the pressure increases. When the pressure was increased above P_C, where T_C goes to zero, the large chiral signal suddenly quenches. This implies that the chiral spin structure completely diminishes as soon as the system loses the long range order, i.e., T_C goes to zero. This is somewhat contradictory to the early neutron scattering result above P_c, where the short range order, so-called partial order, was maintained even above the critical pressure. Quite differently from the pure system, when T_c was suppressed with impurity by substituting Fe in $Mn_{1-x}Fe_xSi$, the chiral signal was much weaker and was observed in smaller temperature range. Interestingly, in contrast to hall data taken under hydrostatic pressure, the chiral contribution in iron doped MnSi is found to have the opposite sign as the anomalous Hall effect.

For the shot noise thermometry, we have so far achieved the resolution of the temperature reading, $\Delta T/T \sim 10^{-4}$ at the liquid Nitrogen temperature with the typical experiment parameters such as gain, bandwidth and integration time, etc. Parallel to the effort to improve the temperature resolution, we devise the shot noise measurement to characterize the measurement chain to determine the overall microwave signal gain and the noise temperature. Considering the fact that the direct method to characterize the measurement chain is quite limited, this opens another potential to use this system not only for measuring the physical temperature but also for an instrumentation to characterize the measurement chain.

Investigation of the Electron Interactions in Graphene

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Funding:	$175,000

PROGRAM SCOPE

The goal of this project is to investigate the exotic physical phenomena associated with the electron interaction in graphene. In particular, we have been focusing our research on fundamental transport properties in high quality graphene samples by probing its correlated electronic states. This effort has been greatly augmented by developing processes to yield high-mobility, homogeneous graphene, and hybrid graphene structures utilizing novel substrate and dielectric engineering employing hexa boron nitride (hBN) to provide material platforms for investigations into possible emergent phenomena. The key scientific questions we are trying to address are (1) searching for highly-correlated fractional quantum Hall effects in the extreme quantum limit; (2) investigating excitonic correlations in double-layer graphene hybrid nanostructures; (3) studying interaction-induced, quasi-relativistic, hydrodynamic thermoelectric transport in graphene at the quantum limit; (4) examining interaction physics in graphene at extreme charge density; and (5) performing bulk magnetic moment measurements of graphene in the IQHE and FQHE regimes. Through this research effort, we are seeking new insights into the unique correlated behavior of electrons in graphene. As the longer term and broader impact, we hope that the discoveries made in this project will provide the basis for making new, low-dimensional structures for electronic devices, and potentially provide insight into emergent properties that will be the basis for energy-efficient material applications.

FY 2012 HIGHLIGHTS

Electronic systems with multiple degenerate degrees of freedom can support a rich variety of broken symmetry states. We have observed quantum Hall effects at all integer filling factors in graphene, consistent with exchange driven quantum Hall ferromagnetism within the combined spin valley isopsin space. Tilted field measurements of the activation gaps associated with the broken symmetry quantum Hall states have allowed us to extract quantitative information about the spin textures of the ground state and its elementary excitations. For the half-filled Landau levels, such as the $\nu = 4$ state, the effective g-factor of the charge carriers can exceed its bare value of 2. Measurements of multiple samples show a correlation between effective g-factor, measured energy gaps, and sample quality. This correlation suggests that the multiple-spin Skyrmionic excitations that serve as charge carriers in these states are disorder limited, with larger Skyrmions forming as sample quality improves.

Mapping the Electron Response of Nanomaterials

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Funding:	$207,000

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 free-standing 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 2012 HIGHLIGHTS

For 1D systems, we have discovered that a monatomic Co on Cu step wire system surprisingly undergoes a CDW instability. This was unexpected since, in general, the electronic structure of the metallic substrate typically strongly interacts with most impurities. However, DFT computations showed that the Co chain is an isolated system. In fact, the mechanism of the 1D CDW instability is novel, as it is driven by correlated spin-exchange interactions. Current and future works on this system are to understand the limits of DFT in predicting this experimental result and whether more advanced techniques such as DFT+*U* or DMFT are able to compensate for DFT's failures for this system. For 2D systems, we are probing the symmetric and anti-symmetric state (1+ and 1-) image potential states in the first Rydberg series using femtosecond 2PPE on Gr/Ir(111). We are currently investigating the 1+ state, which is believed to be an interfacial state between graphene and its Ir substrate, as evidenced by a measured shorter lifetime relative to the 1- state. In addition, we have initiated a study of a new 2D system, viz. MoS_2, which is a direct bandgap material in only its single-layer form but switches to indirect bandgap for 2 or more layers, based on reported optical measurements. We have also started ARPES/STM measurements of a quasi-2D system, 2H-$NbSe_2$, which is a layered transition-metal dichalcogenide. This material exhibits both superconductivity (SC) and an incommensurate 2D charge-density wave phase. Finally, in this upcoming year, we will begin experiments on unoccupied-states in topological insulators, which possess a topologically protected surface state.

Charge Inhomogeneity in Correlated Electron Systems

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Funding:	$110,000

PROGRAM SCOPE

The goal of this project is to develop our fundamental understanding of why high temperature superconductivity exists, while at the same time developing the synthesis of new materials. We are addressing the role of dopant atoms in making a high temperature superconductor. There are two families of high temperature superconductors: layered copper-oxides and layered iron compounds. Both have parent compounds that are magnetic and non-superconducting which are turned into high temperature superconductors by adding dopant ions to the crystal. For the copper-oxides, the parent compounds are insulating and it is clear that dopants are necessary to provide charge carriers to conduct current and superconduct. For the iron compounds, the situation is less clear. The parent compounds are already conducting, and some dopant ions add charge carriers while others only alter the crystal structure. Our program focusses on the parent compound iron-tellurium. A superconductor can be made by replacing some, or all, of the tellurium by selenium—this change does not add charges but changes the structure. We have discovered that iron tellurium can also be made superconducting by adding extra oxygen— in this case, the number of charge carriers does change. We can also add oxygen and charge carriers to iron selenium, though that addition destroys superconductivity. The addition of oxygen only works for iron-tellurium in a film structure, not bulk samples. In the films, oxygen is easily incorporated and reversible; the superconductivity can be turned on and off by simply annealing.

FY 2012 HIGHLIGHTS

We have undertaken an extensive effort to redesign our method of synthesizing superconducting iron-tellurium oxide to allow us to conduct more sophisticated experiments. Initially, our superconducting films consisted of many islands of material which led to very high surface area and easy oxidation. However, the open nature of the films makes many experiments difficult. We have managed to improve the density, smoothness, and crystalline order of our iron tellurium films, though at the cost of making them harder to oxidize. The improved films have been used for detailed crystal structure measurements in collaboration with Dr. Xuerong Liu at the National Synchrotron Light Source at Brookhaven National Laboratory. We observed a collapse in the spacing of the iron planes coincident with superconductivity. We have also conducted neutron scattering experiments revealing that superconducting iron-tellurium oxide is also magnetic in a manner similar to the iron-tellurium parent compound. Investigating the interplay between magnetism and superconductivity will be our major focus next year.

Fundamental Studies of High-Anisotropy Nanomagnets

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Funding:	$84,000

PROGRAM SCOPE

This project is focused on a key class of materials important in magnetism and nanoscience. The specific target is nanometer-length-scale and real-structure control of structures as a means of creating nanomaterials with high magnetic anisotropy and high coercivity. 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 nanoscale clusters and particles, where anisotropic structures and surface effects are expected to lead to new high-anisotropy nanomagnets. Both rare-earth-free and rare-earth-containing Co-Fe-rich systems are explored. The second part is focused on new thin-film nanomagnets and unconventional alloy structures. Here, the goals are to control the coercivity and anisotropy in hexagonal and related structures, where exchange and anisotropy effects of substitutional and interstitial doping are investigated. The third part is aimed at understanding the effects of spatial confinement on magnetic hardening in nanoscale structures undergoing structural transformations. This topic is highly important in magnetic nanomaterials since many of them have to be thermally processed to create nanophases with desired hard magnetic properties.

Symmetries, Interactions, and Correlation Effects in Carbon Nanotubes

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Funding:	$150,000

PROGRAM SCOPE

This program focuses on effects of dissipative environment on carbon nanotube quantum dots, to be probed by low-temperature magneto-transport methods. Tunneling in the Ohmic environment is known to mimic tunneling in the Luttinger liquid—an interacting one-dimensional electron system. The PI's group has recently studied resonant tunneling (i.e., tunneling through an intermediate resonance) between two dissipative leads and observed perfect resonances with vanishing width, predicted by Kane and Fisher in 1992. This program develops the analogy between the Ohmic environment and the Luttinger liquid further, and addresses several quantum impurity problems with interacting leads. The major research directions include (1) mapping the phase diagram of a resonant level in a dissipative environment; (2) the Kondo effect in a dissipative environment, including non-equilibrium properties; (3) studies of non-Ohmic dissipation—beyond the Luttinger liquid analogy; and (4) multi-channel resonant tunneling and the Kondo effect.

The proposed work will enhance understanding of electronic interactions and dissipative phenomena in low-dimensional confined nanostructures, which naturally possess a high degree of symmetry. Interactions and symmetries in confined systems are one of the fundamental topics in modern condensed matter physics.

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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Funding:	$162,000

PROGRAM SCOPE

The scope of our program is to synthesize and characterize the high magnetic-field phase-diagram of the Fe pnictide/chalcogenide superconductors and related compounds. A series of recent studies by us and by other groups suggest the possibility of additional, field-induced phases (akin to the Ferrel-Fulde-Larkin-Ovchinnikov state) in some of the compounds. Our goal is to purify the quality of these and of new materials in order to obtain thermodynamic and spectroscopic evidence for possible additional phases at high fields. For example, in both URu_2Si_2 and LiFeAs, we have found a very anomalous magnetic response within their superconducting state suggesting that these compounds might display chiral-superconductivity responsible for a Cooper-pair orbital moment. However, this is a rather complex project that will require a major experimental effort to unambiguously confirm the existence of such unconventional states.

FY 2012 HIGHLIGHTS

URu_2Si_2 was suggested to be a chiral *d*-wave superconductor with a k_z ($k_x \pm ik_y$) orbital component for the Cooper pair wave-function. This state breaks time-reversal symmetry due to the orbital moment associated with this pair wave-function. Here, we report torque magnetometry in URu_2Si_2 at high fields and very low temperatures revealing a change in the sign of the magnetic hysteresis for $H \rightarrow H_{c2}$, and for angles up to 15^0 away from the *ab*-plane, i.e., from a clear diamagnetic response dominated by the pinning of vortices to a state with a much smaller but "paramagnetic-like" hysteretic response which disappears at H_{c2}. Since diamagnetism results from screening super-currents, we conclude that this anomalous hysteretic response must result from super-currents circulating in the opposite sense which generate an effective moment as expected for a chiral superconductor.

We discovered superconductivity in a new transition metal-chalcogenide compound, i.e., $Nb_2Pd_{0.81}S_5$, with a transition temperature $T_c \cong 6.6$ K. Despite its relatively low T_c, it displays remarkably high and anisotropic superconducting upper critical fields, e.g., $\mu_0 H_{c2}$ ($T \rightarrow 0$ K) > 37 T for fields applied along the crystallographic *b*-axis. For a field applied perpendicularly to the *b*-axis, $\mu_0 H_{c2}$ shows a linear dependence in temperature which, coupled to a temperature-dependent anisotropy of the upper critical fields, suggests that $Nb_2Pd_{0.81}S_5$ is a multi-band superconductor. The static spin susceptibility as calculated through the random phase approximation reveals strong peaks suggesting proximity to a magnetic state and therefore the possibility of unconventional superconductivity.

Infrared Optical Study of Graphene in High Magnetic Fields

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Funding:	$140,000

PROGRAM SCOPE

The goal of this project is to carry out an optical spectroscopy study of graphene and graphene-related materials in high magnetic fields. The intriguing properties of graphene result from its unusual low-energy band structure, rendering the charge carriers in it formally identical to massless relativistic particles. Compared with electronic transport methods, which are dominated by the sample edge in high magnetic fields, optical spectroscopy directly accesses the intrinsic materials properties, yielding important complementary and/or supportive information about the material. The proposed research is focused on studying low-energy electronic structure and many-body interaction effects.

FY 2012 HIGHLIGHTS

Magneto-plasmons in quasi-neutral graphene nanoribbon arrays: In graphene, plasmon, collective oscillation of Dirac electrons, has recently attracted a great deal of attention. For graphene nanoribbons (GNRs), the plasmon frequency depends on the width of the ribbon and the Fermi energy, as well as interaction effects. We employed infrared transmission spectroscopy to study the magnetoplasmons in quasi-neutral epitaxial GNR arrays. The energy of the 0(-1) to 1(0) inter-Landau level (LL) transitions deviates from the characteristic $B^{1/2}$ dependence observed in 2D graphene. This behavior is explained as a signature of the upper hybrid mode formed between the LL transition and the plasmon resonance. Studying this hybrid mode allows us to probe the zero magnetic field plasmon resonance in the interacting regime when coupling to electron-holes excitations results in strong decay of plasmons. For 100-nm-width GNRs, we observe a wavelength shrinkage of 170, a value difficult to achieve in common plasmonic materials but in agreement with that predicted for graphene.

Magneto-phonon resonance in grapheme: In graphene, long-wavelength optical phonons (E_{2g} phonons) can be absorbed by electrons, resulting in renormalization of phonon frequencies and line broadening. Specifically, the G peak in Raman spectra is predicted to exhibit anti-crossing behaviors when the E_{2g} phonon energy matches the separation of two LLs. We performed polarization-resolved Raman spectroscopy on graphene in magnetic fields up to 45 T. This reveals a filling-factor-dependent, multi-component anti-crossing structure of the Raman G peak, resulting from magneto-phonon resonances between magneto-excitons and circularly polarized E_{2g} phonons. This structure can be explained with a model of Raman scattering taking into account the effects of spatially inhomogeneous carrier densities and strain. This model shows that random fluctuations of strain-induced pseudo-magnetic fields lead to increased scattering intensity inside the anti-crossing gap, consistent with the experiment.

Microwave Spectroscopy of 2D Electron Solids: Fractional Quantum Hall Effect and Controlled Disorder

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Funding: $120,000

PROGRAM SCOPE

Using microwave spectroscopy, we study pinning modes of electron solids related to the Wigner crystal, which occur in 2D electron systems (2DES) at high magnetic fields and low temperatures. Pinning modes are small oscillations of carriers within the pinning potential; so they are disorder-induced. Pinning modes produce rf or microwave resonances in the conductivity spectrum and are ubiquitous in sufficiently low disorder 2DES in high magnetic field, for phases with spatially periodic charge density order. One part of the proposed work concerns solids concomitant with the fractional quantum Hall effects (FQHEs), and in particular FQHEs in the first excited Landau level, to study phases near 5/2 which are of current interest. This first part of the work focuses on the cleanest possible samples. The second part of the work is to study the pinning mode resonance in samples with deliberately-introduced, well-characterized alloy disorder, to better understand how the disorder and aspects of the resonance are related and to gain a better fundamental understanding of the pinning mode.

FY 2012 HIGHLIGHTS

We have characterized the pinning modes of several samples in which the 2DES resides in dilute $Al_xGa_{1-x}As$ alloy, with x between 0.21 and 0.85%. We find that a resonance fitting the description of a pinning mode is present for each of the samples. Intriguingly, a simple model (neglecting localization and correlations) for the disorder effect on the 2DES cannot explain the resonance frequency. In collaboration with Mansour Shayegan, we have also studied pinning modes in wide quantum wells, for which both electron-electron interaction and disorder are different from more samples studied earlier. We have found a pinning mode of what appears to be a novel electron solid phase, which can exist quite close to Landau filling of $\nu=1$.

Fe Pnictide and f-Electron Novel Materials/Magnetism, Superconductivity, and Quantum Criticality

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PROGRAM SCOPE

This work will prepare high quality single and polycrystalline samples of iron-based superconductors, as well as novel f-electron quantum critical systems. These samples will be characterized by x-ray diffraction, electrical resistivity, magnetic susceptibility, and specific heat over a broad range of parameter space—between 0.05 K and room temperature and in magnetic fields up to 20 T routinely, and 45 T upon need. Measuring the specific heat of the iron superconductors as a function of magnetic field, as well as vs angle in field, will aid in determining the nodal structure of the superconducting gap. The goals of the work are to prepare and characterize new, as well as known, systems of interest that help understanding of the unusual superconducting, magnetic, and quantum critical behaviors in these materials.

FY 2012 HIGHLIGHTS

Using measurements of the specific heat in magnetic field of the iron-based superconductors $BaFe_2(As_{0.7}P_{0.3})_2$ and $Ba(Fe_{1-x}Co_x)_2As_2$, and with strong theoretical collaboration, we were able to show the importance of a multiband approach in understanding these materials. In the Co-doped material, for x=0.10 and 0.13, our data argued for strong interband coupling; while for the P-doped material, our data were found to be consistent with nodes on one of the band gaps. Using zero field specific heat measurements of single crystal samples of $Ba(Fe_{1-x}Co_x)_2As_2$ made by our lab with nine different values of Co-doping, we showed that the behavior of the discontinuity in the specific heat at T_c, ΔC, is the same whether there is coexistent magnetism ($x<0.08$) or not ($x>0.08$).

Heavy Fermions, Quantum Criticality, and Unconventional Superconductivity in Filled Skutterudites and Related Materials

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Funding:	$109,000

PROGRAM SCOPE

Filled skutterudites are technologically important materials for thermoelectric applications. Their potential applications are closely related to the unique crystal structure, which offers also insights into new states of matter and phenomena. The essential ingredients of this structure are loosely bound rare earth atoms in oversized cages formed by pnictogen atoms. At high temperatures, physical properties are determined by almost free magnetic moments of rare earths. At low temperatures, 4f-electrons of rare earths yield unique states of matter and behaviors. These behaviors can be finely tuned by partially substituting one rare earth element for another, without changing the crystal structure or lattice parameters. Alloying allows us to investigate how novel states of matter are related to more conventional ones, which are better understood. In-house synthesized and characterized materials are studied by bulk-type techniques, specific heat, and magnetic susceptibility.

FY 2012 HIGHLIGHTS

During the current funding period, the emphasis was on unconventional superconductivity of $PrOs_4Sb_{12}$, the most interesting and controversial heavy fermion superconductor. The superconductivity is most likely due to quadrupolar fluctuations; $PrOs_4Sb_{12}$ is one of only two known materials with two superconducting transition temperatures. Our results provide strong evidence for the intrinsic nature of both superconducting transitions, contrary to the current consensus. We find that the upper temperature superconducting anomaly in the specific heat is anomalous and is reduced much quicker by any type of alloying than the lower temperature anomaly. We have discovered also an unusually strong correlation between unconventional superconductivity and atomic disorder, as measured by electrical resistivity. In collaboration with S. Julian (Toronto) and A. McCollam (Nijmegen), we continued comprehensive study of this system via quantum oscillations in a wide range of magnetic fields. We have discovered that field-induced antiferroquadrupolar state is strongly modified by hyperfine interactions.

Time-Resolved Synchrotron Studies of Spin and Charge Dynamics in Solids

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Funding:	$44,000

PROGRAM SCOPE

A unique facility for time-resolved far-infrared spectroscopy at the National Synchrotron Light Source is being used to study spin and charge dynamics in superconductors and semiconductors. This facility has the capability to study time-dependent phenomena using laser pump and broadband infrared probe. The probe photon energies may be varied continuously from far infrared (1.2 meV; 300 GHz; 10 cm^{-1}) through the visible and even into the ultraviolet (greater than 5 eV; 1200 THz; 40,000 cm^{-1}). Temporal resolution is ~ 200 ps, and the pump/probe repetition rates can vary from 19--180 ns. A 10 T magnet is also available for measurements. This project uses these unique facilities to study the recombination process of quasiparticle excitations in superconductors, photoprocesses in interesting materials, and the dynamics of photoexcited carriers in semiconductors.

FY 2012 HIGHLIGHTS

Quasiparticle recombination in a superconductor with an s-wave gap is typically dominated by a phonon bottleneck effect. We have studied how a magnetic field changes this recombination process in metallic thin-film superconductors, finding that the quasiparticle recombination process is significantly slowed as the field increases. While we observe this for all field orientations, we have focused on the results for a field applied parallel to the thin film surface, minimizing the influence of vortices. The magnetic field disrupts the time-reversal symmetry of the pairs, giving them a finite lifetime and decreasing the energy gap. The field could also polarize the quasiparticle spins, producing different populations of spin-up and spin-down quasiparticles. Both processes favor slower recombination; in our materials, we conclude that strong spin-orbit scattering reduces the spin polarization, making gap reduction dominate.

Microwave- and Terahertz- Photo-Excited Transport in the Two Dimensional Electron System

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PROGRAM SCOPE

Magneto-transport studies of low dimensional systems have contributed to exciting new advances in condensed matter physics, such as the integral and fractional quantum Hall effects observed in the GaAs/AlGaAs two-dimensional electron system, and the identification of Dirac fermions in graphene. Such magneto-transport studies have mostly examined the equilibrium properties of the above mentioned low dimensional electron systems. This research is concerned with examining magneto-transport under steady-state non-equilibrium conditions attained under microwave- and terahertz-photoexcitation of the low dimensional electron system based on GaAs/AlGaAs and graphene. The aim of the study is to uncover novel emergent phenomena in far-from-equilibrium systems. An example of such emergent phenomena in the GaAs/AlGaAs system is the microwave-radiation-induced zero-resistance state, where the diagonal resistance vanishes under photo-excitation in the presence of a transverse magnetic field, without Hall resistance quantization.

FY 2012 HIGHLIGHTS

The influence of the microwave linear polarization on the microwave radiation-induced magnetoresistance oscillations, which lead into the radiation-induced zero-resistance states, has been a topic of intense interest because existing theories have made differing predictions regarding the role of the microwave polarization. Some theories have predicted polarization insensitivity, while others have implied a strong polarization sensitivity in the microwave radiation-induced transport. To investigate the problem, we developed a setup using circular waveguides and home-made microwave launchers, where the microwave linear polarization could be rotated with respect to the sample, from outside the cryostat. The setup was then applied to investigate the polarization sensitivity problem. The results showed a striking linear polarization sensitivity that helped to identify the relative strengths of proposed mechanisms for the oscillatory magnetoresistance induced by microwave excitation.

Microwave photo-excited transport has also been investigated in epitaxial graphene – graphene realized by the controlled evaporation of silicon from the surface of silicon carbide. Unexpectedly, measurements revealed a strong microwave sensitivity in the dc-response mono- and tri-layer epitaxial graphene. In addition, hole spin resonance was observed; and this could be followed as a function of the microwave frequency and temperature. The results helped to demonstrate resistive detection of spin resonance in nanoscale epitaxial graphene devices, identify the operative mechanism in resistive resonance detection, and provide a measurement of the g-factor, the spin relaxation time, and the sub-lattice degeneracy-splitting in the absence of a magnetic field.

Spin Polarized Electron Transport through Aluminum Nanoparticles

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PROGRAM SCOPE

The goal of the project is to understand the physics of single, nanometer scale ferromagnetic particles, in the regime of quantized electronic energy levels because of the confinement, as well as to learn the physics of interplay between electron transport and magnetism in devices containing such particles. A variety of techniques to probe the particles, such as electron tunneling, microwave pumping, measuring ferromagnetic properties versus different ferromagnetic material, and spin-transfer torque (STT), were proposed in order to accomplish the goal. The understanding of the coupling between the electrons and the magnetization is important because this coupling sets the limit in miniaturization of devices in spin-electronics.

FY 2012 HIGHLIGHTS

Significant advance in understanding of the coupling between electron transport and magnetization in single Co particles of diameter 1-2 nm have been obtained. The combination of tunneling measurements at cryogenic temperatures and our theoretical modeling lead to the conclusion that the coupling is governed by the intrinsic Spin-Orbit (SO) coupling in the particle and its fluctuations among different discrete levels. In particular, the fluctuations of the magnetic anisotropy energy of the particle, among the discrete levels, cause the coupling between electron transport and the magnetization to become much stronger than in the bulk and probably impossible to control. A simple theoretical model was developed, accounting for both quantitative and qualitative observations, while none of the prior models is consistent with our measurement. One consequence of our findings is the implication that STT torque cannot be observed in a Co particle in a double barrier device, in agreement with our experimental trials. The reason is that the noise caused by the SO-fluctuations among discrete levels is much larger than the coherent part of the coupling (STT), so the fluctuations will simply obliterate any STT. The focus needs to be to investigate electron transport through ferromagnetic particles with much weaker intrinsic spin-orbit coupling, such as Permalloy or rare-earth.

In addition to the finding described above, we have observed very large electron-in-a-box g-factors in a Co particle (close to 6). Such large g-factors have not been measured yet in metallic particles, where the g factors were always less than 2, except in some peculiar theoretical situations where they can be slightly larger than 2. The large g-factor is an electron-electron interaction phenomenon, which leads to the violation of the spin-selection rules in single electron tunneling.

Electron Imaging in Graphene

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PROGRAM SCOPE

Graphene is an exciting new material with electronic properties that are very different from conventional semiconductors. Electrons and holes travel at a constant speed that is independent of energy, and there is no energy gap—the conductance and valence bands join at a point. Visualizing the motion of electrons and holes in graphene will be important to understand the science and to develop new types of devices.

Westervelt's group is using a custom made liquid-He cooled scanning probe microscope (SPM) to image electron motion through graphene devices. The conducting SPM tip acts as a movable gate that changes the electron density immediately below. This change can deflect electron waves, altering their transmission through a device and allowing one to image electron flow by displaying the conductance change as the tip is scanned above a sample. The tip-induced density change can also be used to tune the number of electrons on a quantum dot, permitting one to create a single-electron transistor, and to do Coulomb blockade spectroscopy on individual quantum states. Bell's group is fabricating atomic scale graphene devices for this research by sculpting a suspended graphene sheet with the electron beam of a high-resolution transmission electron microscope. Using this approach, one can both cut the sheet and image the resulting device with atomic spatial resolution.

FY 2012 HIGHLIGHTS

Westervelt's group has developed a new approach to probe electrons inside an atomic scale graphene device, based on Ashoori's earlier work at MIT. A voltage applied to a conducting SPM tip induces an image charge inside a graphene device immediately below. This image charge can be sensed with high sensitivity by using a custom-made capacitance bridge and cooled charge amplifier mounted adjacent to the SPM tip. Using this approach, they are able to probe a nanosculpted graphene quantum dot and use Coulomb blockade spectroscopy to measure its quantum states, without the need to create external source and drain leads.

Westervelt's group has also developed coaxial and triaxial SPM tips that provide improved spatial resolution. The conducting core of a coaxial SPM tip is surrounded by a grounded, conducting shell. Field lines escape through an opening at the sharp end, producing a dipole field profile that is sharper than the profile of an unshielded tip. A triaxial SPM tip has both inner and outer conducting shells, with the outer shell grounded. By applying voltages of opposite sign to the core and inner shell, one can create a field profile that has a sharp zero above the end of tip, in open space, which has spatial resolution sharper than the tip radius.

Quantum Materials at the Nanoscale

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Funding:	$1,849,000

PROGRAM SCOPE

The central aim of the Quantum Materials at the Nanoscale (QMN) cluster is to explore the collective organization and dynamics of charges, spins, orbitals, and ions that arise at the nanoscale in a broad class of important, correlated electronic materials.

FY 2012 HIGHLIGHTS

(1) Tunable superconductivity in island arrays and nanowires: Mason and Goldbart demonstrated that systems of mesoscopic superconducting islands placed on normal metal films can behave as disordered two-dimensional superconductors, where the superconducting transitions can be tuned via island size, spacing, and configuration. They performed the first systematic measurements of the dependence of the superconducting transitions on island spacing, and showed that the island systems seem to approach a quantum metallic state, a state previously thought to be precluded in 2D because of localization. The results were published in *Nature Physics*.

(2) Interplay of superconductivity, magnetism, and spin-orbit coupling in heterostructures: Hughes and Vishveshwara theoretically studied the effects of strong electron correlations in the 2D materials and proposed viable experiments in heterostructure devices in which fractional charge, the quantum Hall effect, or Majorana fermions can be realized. They predict that a magnetic spin-density wave state can be induced on the edge of the quantum spin Hall effect in the presence of repulsive electron-electron interactions. Hughes and Vishveshwara have also shown that a layered sandwich structure with a ferromagnet between two 3D topological insulators will produce an integer quantum Hall effect due to the appearance of chiral fermion modes on the lateral sides of the magnetic layer.

(3) Imaging nanoscale magnetic stripe formation in Mn_3O_4: To image the nanometer-scale magnetic domains that develop through the various magnetostructural phases in Mn_3O_4, Budakian has applied variable temperature cantilever magnetic force microscopy (MFM) to investigate the real space evolution of the high temperature incommensurate phase of Mn_3O_4 to the low temperature commensurate phase. Results indicate that, at low temperatures, the system phase separates into striped regions with a characteristic lengthscale of order 100 nm. In this field range, Raman spectroscopy measurements by Cooper and x-ray measurements by Abbamonte indicate coexistence between tetragonal and orthorhombic phases. The local information provided by the MFM data has shown, for the first time, that the coexistence region consists of a periodic arrangement of spins in which the spatial modulations have a well-defined orientation with respect to the crystallographic directions.

(4) Two-stage orbital ordering in $KCuF_3$: Raman scattering measurements by Cooper and x-ray scattering measurements by Abbamonte uncovered a previously unidentified structural phase transition in $KCuF_3$. To explain this observation, Goldbart proposed a model that includes a new, direct orbital exchange term, whose effect is to create a near degeneracy between spin/orbital configurations that dynamically frustrates the spin subsystem but is lifted at low temperature by orbital–lattice interactions. These results were published in *Nature Physics*.

Competing Interactions in Complex Transition Metal Oxides

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Funding:	$120,000

PROGRAM SCOPE

The “heavy” 4d and 5d transition elements (TE) have more extended d-orbitals compared to 3d electron materials. Stronger p-d hybridization, spin-orbit (SO) and electron-lattice couplings, and reduced intra-atomic Coulomb U and crystalline electric field (CEF) interactions generate competitions between metallic and insulating states or paramagnetic and magnetic order. Small variations of composition, pressure, or applied fields can induce drastic changes in the varied ground states exhibited by TE oxides (ferroelectric, orbital or magnetic order, superconductivity, density waves), as well as control technologically important phenomena such as colossal magnetoresistance (CMR) and giant magnetoelectric effects (GME).

We are investigating perovskite variants $ABO_{3-\delta}$ (A=Ca,Sr,Ba; B=Mn,Fe,Ru) and R-type ferrites $(Ba,Sr)M_{2\pm x}Ru_{4\pm x}O_{11}$ (M=Fe,Co,Mn,Ti). Fe-bearing examples of both phases exhibit a rare coexistence of long-range ferromagnetic (FM) order accompanied by narrow-gap semiconducting properties at temperatures above 400 K.

Our research is focused in the following areas:

(1) The rarity of room-temperature, FM semiconductors remains an obstacle to development of spin-polarized semiconductor devices for spintronics. We are identifying fundamental physical and chemical factors that govern the occurrence of FM order above room temperature in ferrite and perovskite phases.

(2) Some perovskite materials appear to exhibit a rare coexistence of magnetic and electric polarizations on the same B lattice sites, and various R-type ferrites show evidence for coexisting magnetic and electric polarizations, whose interplay can be controlled by modest applied fields or electric currents. We are verifying these coexistent phenomena and exploring their ramifications for potential devices.

(3) Both ferrites and perovskites exhibit highly anisotropic physical properties that can be sensitively controlled by varying the relative concentration of 3d versus 4d or 5d elements, which we intend to show adjusts the strengths of the CEF and SO interactions that compete with magnetic frustration and other fundamental interactions to determine the wide-ranging ground states exhibited by these materials.

(4) We take an integrated, interdisciplinary approach to the discovery and characterization of novel TE oxides whose physical properties reflect competing interactions. We synthesize and identify novel materials, grow bulk single crystals to comprehensively study physical properties relevant to

fundamental theories, as well as fabricate and study thin films and heterostructures relevant to device applications.

(5) Our broad expertise and technical assets permit comprehensive investigations of electrical transport, magnetic, dielectric, and thermodynamic properties over a wide range of temperatures $0.05 < T < 1000$ K and magnetic fields $0 < \mu_o H < 14$ T, and high-pressure electrical resistivity and magnetic moment measurements to 10 GPa. We are using National Laboratory facilities and/or external collaborators to conduct EXAFS, and magnetic soft x-ray and neutron scattering experiments to characterize small single crystals and thin films that are not easily studied via conventional electrical transport, magnetic or optical techniques

Quantum Transport in Thin Film Correlated Insulators

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Students:	1 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$185,000

PROGRAM SCOPE

Our experimental program is focused on the magneto-transport, non-equilibrium relaxation, and spin-resolved density-of-states properties of highly disordered two-dimensional electron gases. In particular, we are studying electron correlation effects in two separate but related systems. The first is non-magnetic ultra-thin Be films that are produced by e-beam deposition onto liquid nitrogen cooled glass substrates. Beryllium forms non-granular films that are homogeneously disordered on length scales greater than ~1 nm. The films exhibit a multifold negative magneto-resistance deep in the correlated insulator phase that is associated with a field suppression of the Coulomb gap. Interestingly, the high-field resistance is asymptotic to the quantum resistance h/e^2, suggesting the emergence of a novel *quantum metal* ground state.

The second class of systems we are investigating are ferromagnetic/paramagnetic bilayers which exhibit a proximity-induced exchange field. We have primarily focused on EuS-Al and EuS-Be bilayers, where EuS is a ferromagnetic semiconductor. The bilayer geometry allows us to produce a tunable exchange field in the Be and Al components. The nature of the exchange field and its influence on the spin properties of the non-magnetic components are being studied as a function of disorder, and external magnetic and electric fields.

FY 2012 HIGHLIGHTS

We completed two major experiments last year. The first was a study of the effects of disorder on the exchange field in the Be component of EuS-Be bilayers. We showed that the exchange field survives in very high resistance Be films and, in fact, appears to be relatively insensitive to disorder. We exploited this fact to produce a giant low-field magnetoresistance in the correlated insulator phase of Be films with sheet resistances well above the quantum resistance. This work was published in *Physical Review Letters*. In the second project, an electric gate was added to the bilayers with the goal of producing an electric field modulation of the interfacial coupling between the two components of the bilayer. Specifically, we used the superconducting properties of the Al to directly probe the induced exchange field in the Al layer as function of gate voltage. This strategy was, in fact, successful, and we were able to demonstrate a few percent modulation of the exchange field with rather modest gate voltages. This work represents our first steps toward the ultimate goal of producing a device with a gate controlled internal magnetic field. A manuscript reporting these results is currently under review at *Physical Review Letters*.

Infrared Hall Effect in Correlated Electronic Materials

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Funding:	$149,000

PROGRAM SCOPE

The goal of the program is to develop an understanding of the electronic structure of important novel materials with a focus on the cuprate high temperature superconductors and topological insulators. The technique employed is THz magneto-optics, which has been pioneered by the PI. Polarization modulation techniques allow measurements of the Faraday (or Kerr) rotation and circular dichroism with unprecedented sensitivity. They will be performed at THz frequencies below any energy gaps, pseudogaps, or interaction energy scales so that the states near the Fermi energy are probed. These measurements will be critically compared with transport measurements, Angular Resolved Photoemission Spectroscopy (ARPES), and conventional optics. The goal of the work on the cuprates is accounting for the transport properties of the cuprates in terms of the Fermi surface information available from ARPES with particular emphasis on the underdoped cuprates where quantum oscillations have been observed. We will assess the extent to which Fermiology of the cuprates provides a workable description of their transport and infrared properties. In work on topological insulators, a predicted new quantum state of matter, our goal is to characterize the predicted topologically protected non-degenerate chiral surface states. These surface states are predicted to have exotic properties including Majorana fermions induced by the proximity effect with superconductors.

FY 2012 HIGHLIGHTS

We have significantly improved the sensitivity of our magneto-optical measurement system to permit measurements of small Faraday and Kerr rotation signals encountered in these materials. This has included stabilizing the THz laser system, improving the waveplate rotator, and developing sample gating techniques for signal averaging. These improvements have led to rotation sensitivities of approximately 20 μrad, which is about a factor 10 better than the state of the art.

THz magneto-optical measurements were performed on epitaxial films of the topological insulator Bi2Se3 capped with a layer of the In2Se3. Gated measurements were shown to provide an effective characterization of buried topological metallic interface states. Evidence was found of a shift in Dirac cone due to the trivial insulator/Bi2Se3 interface in comparison with the surface states at the vacuum/Bi2Se3 interface measured by ARPES. These results demonstrate the possibility of passivating the interface and shifting the Dirac cone by capping, which provides a new flexibility in tailoring topological surface states. Also, the energy scale of potential fluctuations was measured at the Dirac point and the conduction band edge. The topological surface state scattering rate was measured from the Dirac point to above the conduction band edge, providing a map of the interplay of the surface state carriers with potential fluctuations and bulk carriers.

Measurement of Single Electronic Charging of Semiconductor Nano-Crystal

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Funding:	$150,000

PROGRAM SCOPE

The goal of our research is to understand the transport mechanism of electrons in arrays of semiconductor quantum dots. At nanometer sizes, the optical absorption and emission of semiconductor nano-crystals, and the exquisite control over their size, demonstrated by our chemist collaborators, provide control over the optical properties of large numbers of quantum dots. This has already led to high efficiency LEDs. The promise of increased efficiency of solar cells, by using a larger portion of the solar spectrum, has stimulated great interest in the electron transport properties of arrays of these nano-crystals, which are much more poorly understood than the optical ones. We work with the group of Professor Bawendi of MIT to fabricate arrays of nano-crystals. The nano-crystals, which are synthesized in solution, self-assemble into hexagonal close-packed arrays. In addition to the potential application to solar cells, these arrays provide a model system for the Hubbard model, one of the most important Hamiltonians for understanding strongly interacting electron systems.

FY 2012 HIGHLIGHTS

Earlier work, by both our group and others, has shown that although one can deposit films of semiconductor nano-crystals, with hexagonal close-packed order, the order extends only over distances of order micrometers. In addition, to make the films have measurable conductance, even with many squares in parallel, one needs to anneal or chemically treat them; and this leads to cracking of the films. We recently published results showing that we can pattern crack-free nano-crystal films on the nanometer length scale and measure the current through them. In addition to strong photo-luminescent efficiency, these films have a higher current for a given voltage and geometry than the large area films studied previously. The most surprising feature of these nano-patterned films has been observed in the past few months: the current at fixed voltage shows huge fluctuations with time. The fluctuations scale approximately linearly with the average current as we increase the voltage. We find that the frequency (f) dependence of the fluctuations is approximately 1/f, which is common to many materials and phenomena; but the surprising aspect is that the magnitude of the fluctuations is 100% at $f \sim 10^{-4}$ sec. Random fluctuations grow rapidly with temperature T above about 150 K and usually are below the amplifier noise below this T. However, we sometimes observe telegraph noise at low T. All these results suggest that the current flows through a small number of, perhaps only one, filamentary path. We have patterned a charge-sensing transistor adjacent to the nano-crystal sample, which will allow us to better characterize the conducting filaments.

Novel Temperature Limited Tunneling Spectroscopy of Quantum Hall Systems

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Funding:	$175,000

PROGRAM SCOPE

Low-dimensional electronic systems in semiconductors and in graphene have proven to be a remarkable testing ground for the physics of highly correlated states, such as the quantum Hall effects, edge states, and Wigner Crystallization, all of which have been extensively studied through transport measurements. However, most transport measurements are only sensitive to the structure of the system near the Fermi energy, missing rich structure away from it. We have developed a new tunneling method for measuring energy levels in low-dimensional electronic systems in which it was previously impossible to obtain such data. Moreover, the new technique has extraordinary energy resolution, ultimately limited only by the sample temperature. The method is called *Time Domain Capacitance Spectroscopy* (TDCS), and we have successfully applied it to semiconductor systems. We are working to apply TDCS to a variety of systems so that we may study novel physics arising from interactions of electrons with a magnetic field or from interaction of electrons with each other to produce highly correlated electronic states.

FY 2012 HIGHLIGHTS

TDCS requires the development of samples containing the electronic system of interest sandwiched between two other layers. One of these layers acts as a blocking barrier for electrons; the other permits electron tunneling to a nearby electrode. We have been experimenting with layered samples made by using hexagonal boron nitride (hBN) layers as the blocking and tunnel barriers. Working with Pablo Jarillo-Herrero at MIT, we have fabricated tunneling heterostructures comprised of graphene on hBN substrates and tunnel barriers constructed of exfoliated hbN. In magnetic field, we studied planar tunneling into graphene and observed spectra from a series of Landau levels. While these measurements give basic qualitative information, performing TDCS measurements will allow us to probe insulating states and will give us highly quantitative results. We have also made capacitance and transport measurements on layers of graphene on top of hBN on top of graphite. The graphite layer provides an extremely flat substrate for the hBN and a very flat surface for the graphene. Moreover, we can measure capacitance of sub-micron samples tailored to avoid defects. These ultra-clean samples produced remarkable results. In perpendicular fields greater than 1 Tesla, we observe a quantum Hall state at the charge neutrality point. However, with application of strong field parallel to the plane of the graphene, the longitudinal conductivity increases from zero and approaches twice the quantum conductance. Capacitance measurements show that the sample interior remains insulating, consistent with a “quantum spin-Hall insulator,” with electrons of opposite spins propagating in opposite directions in quantum channels at the edge of the sample. The sample acts similarly to a “topological insulator” but in a situation with high magnetic fields applied when time reversal symmetry is broken.

Probing Nanocrystal Electronic Structure and Dynamics in the Limit of Single Nanocrystals

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Funding:	$235,000

PROGRAM SCOPE

This project focuses on the basic understanding of the optical physics of semiconductor NCs. We propose to use, in large part, single NC spectroscopy to directly probe exciton and multiexciton spectroscopy and dynamics in a variety of NCs and NC hybrid structures.

The project consists of a set of critical and ambitious studies of nanocrystal electronic structure and dynamics, including (1) probing the single NC spectroscopy and dynamics of near infrared NCs of PbS, PbSe, and InAs, for the first time, using a newly developed photon counting detector technology that is sensitive to the 1-2 micron range; (2) probing the relationship between the "Auger" mechanism, thought to be responsible for most of the fast dynamics in multiexcitons and charged excitons, and fluorescence intermittency, from room temperature down to cryogenic temperatures; (3) probing the spectral dynamics of single NC's using photon correlated fourier transform spectroscopy (PCFS) as a function of temperature to determine the role of phonons, dynamic Stark effects, and surface or matrix effects in spectral lineshapes and spectral diffusion. We are developing PCFS as a sensitive and powerful method to measure the dynamics of the spectral correlation of single NC that are isolated on a substrate and combined with fluorescence correlation spectroscopy, to study the average single NC spectral correlation dynamics directly in solution.

FY 2012 HIGHLIGHTS

We have made much progress in increasing our sensitivity and time range in our PCFS set up. We have two separate directions. (1) We are combining PCFS with FCS, which we call Solution-PCFS or S-PCFS, which allows us to measure the average single NC spectral correlation line shape directly in solution. We have used S-PCFS to measure the average spectral line width of NCs across multiple materials and, for CdSe-based NCs, across multiple synthetic schemes. We have found that the single NC linewidth is remarkably similar for all materials studied (CdSe, InP, InAs). We have also found that there is a clear correlation between linewidth and the thickness of a CdS shell on CdSe NC. (2) We have taken PCFS to cryogenic temperatures and have measured the onset of spectral diffusion as a function of time. We find that the single NC linewidth is ~0.01 meV at relatively fast time scales (<0.01 msec) and that we can watch the onset of spectral jumps that broaden the linewidth.

Quantum Transport in Topological Insulator Nanoelectronic Devices

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Funding:	$152,000

PROGRAM SCOPE

This research program is 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.

FY 2012 HIGHLIGHTS

Photocurrent in TIs: In a collaborative effort between the Gedik and Jarillo-Herrero groups, an experiment was designed to measure photocurrents induced by circularly polarized light in electronic devices fabricated using exfoliated crystals of low bulk density Bi_2Se_3. A photocurrent was discovered that reverses direction upon changing the light polarization from left- to right-circularly polarized. These results are consistent with the surface state spin-distribution revealed by ARPES, confirming the surface nature of these currents. The results were recently published in *Nature Nanotechnology*.

High Field Magnetoconductance: To study some of the more exotic features of the TI surface channel, it is desirable to achieve high mobility surface transport. However, gate-tunable devices reported so far are limited to surface mobilities around 1,000 cm^2/Vs. We address this challenge by developing a novel fabrication approach based on mechanical transfer of ultrathin layers of hexagonal Boron-Nitride (hBN) to cover the Bi_2Se_3 device. Using this technique, we have recenlty fabricated devices with surface mobilities exceeding 3,000 cm^2/Vs. These devices, measured in high magnetic fields, exhibit two sets of Shubnikov de Haas (SdH) oscillations: a prominent set associated with the 3D bulk Fermi surface and a smaller, “secondary” set of oscillations associated with the surface. Progress in this direction will allow us to address a number of open scientific problems, including the behavior of quantum oscillations in the presence of both bulk and surface carriers and the potential for observing the quantum Hall effect in Bi_2Se_3 in a certain regime of thickness, high magnetic field, and tunable carrier density.

Capacitance Measurements: To single out the surface contribution on the background of the bulk, we began studying the surface capacitance. Capacitance is sensitive to the ground-state density of states which is manifest as a correction, called *quantum capacitance*. It is a valuable probe which has not been employed to studying the TI surface yet. Our preliminary results confirm the existence of a non-monotonic density of states which we associate with the surface states.

Magnetic Nanostructures and Spintronic Materials

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Funding:	$80,000

PROGRAM SCOPE

The scope of this project is to continue exploring magnetodynamics and magnetostatics in spintronic related materials, coupled nanostructures, bio-related nanoparticles, and single crystal Fe. Spintronic materials to be examined are single crystal $Co_{1-x}Fe_xS_2$ particles and powders in collaboration with Chris Leighton at Minnesota and Fe_3O_4 single crystal films on MgO (100) in collaboration with Casey Miller at South Florida. Coupled nanostructure systems are perpendicularly oriented multilayer nanostructures in collaboration with Eric Fullerton at UC–San Diego, laterally exchange coupled nano-structures in collaboration with scientists at Hitachi Storage Technologies, and anti-dot structures in collaboration with Lance DeLong at Kentucky. We are examining bio-related nanoparticles in collaboration with Josep Nogues in Barcelona, Spain, and Zach Hilt at Kentucky. Our investigation on damping and its relation to transport in transition metal is being done in collaboration with Dan Dahlberg at Minnesota. The primary tool utilized in these studies is ferromagnetic resonance, which has been enhanced by a more powerful and sensitive microwave source implemented in this project period.

FY 2012 HIGHLIGHTS

We are preparing the results on $Co_{1-x}Fe_xS_2$ powders for publication and will be presenting Fe_3O_4 results at the upcoming MMM meeting. A paper on continuous multilayer films with perpendicular interface anisotropy has been submitted, and measurements have begun on such films laterally constrained. Another paper has been submitted on anti-dot structures, and simulations of coupled nano-wires are being done prior to production of optimal structures. Measurements on hard/soft, core/shell nanoparticles are underway, the results of which are quite intriguing. The damping/transport project has switched from Ni to Fe single crystal films to avoid magnetostriction and reduce damping effects. The enhanced power and signal purity of the new microwave source is proving invaluable in conducting the above experiments. The PI gave five invited talks this fall in Colorado, Wyoming, and Wisconsin at universities and a national lab and talked to students in high school science classes in Wisconsin.

Novel Behavior of Ferromagnet/Superconductor Hybrid Systems

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Funding:	$165,000

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 better understand the signatures of the LRTC in a variety of experimental situations, as well as how to optimize and control generation of the LRTC.

FY 2012 HIGHLIGHTS

Early on, we discovered that we could enhance the magnitude of the LRTC by magnetizing our Josephson junction samples. In collaboration with the groups of Julie Borchers and John Unguris at NIST, Maryland, we showed that this enhancement was due to a “spin-flop” transition in the synthetic antiferromagnet we used in the middle of our samples. Those results were published in Physical Review Letters in 2012. More recently, we have studied how the maximum supercurrent that can pass through our Josephson junctions depends on the area of the junction. The results provide indirect evidence that the junctions have an exotic ground state where the phases of the two superconductors differ by $\pi/2$. We are currently following up those studies with an experiment that can measure the phase difference directly. We have also introduced a ferromagnetic multilayer with perpendicular anisotropy into our samples. That development enables us to optimize generation of the spin-triplet supercurrent without the need for magnetizing our samples, as was the case in the past. We are currently trying to fabricate samples where we can control the LRTC by rotating the direction of magnetization of one of the three ferromagnetic layers in the device. Finally, we are working toward fabricating Josephson junction samples with planar geometry to explore the maximum range of the LRTC.

Probing High Temperature Superconductors with Magnetometry in Ultrahigh Magnetic Fields

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Funding: $230,000

PROGRAM SCOPE

The objective of this research is to investigate the high-field magnetic properties of high temperature superconductors, materials that conduct electricity without loss. A technique known as high-resolution torque magnetometry will be developed to directly measure the magnetization of high temperature superconductors. This technique will be implemented using the 100 Tesla pulsed magnetic field facility that is part of the National High Magnetic Field Laboratory at Los Alamos National Laboratory. This research will address unanswered questions about the interplay between magnetism and superconductivity, determine the electronic structure of high temperature superconductors, and shed light on the mechanism of high temperature superconductivity and on potential applications of these materials in areas such as energy generation and power transmission.

FY 2012 HIGHLIGHTS

Our supported research started on July 1, 2012. Between July 1 and September 30, our research focused on the development of the experimental techniques. We designed micro-cantilevers using insulating plastic foils. The new design provides us cantilevers with spring constant in the range of 10^{-2} N/m to 10^{2} N/m. We also succeeded in fabricating devices with wire loops on our cantilevers. Passing a DC current through the loop, we generated a magnetic moment on the cantilever, offering a direct calibration of the spring constant of the cantilever under an external magnetic field.

In August, we visited the Los Alamos National Laboratory to use the pulsed magnets to test our experimental methods in the Pulsed Magnetic Field Facility of the National High Magnetic Field Laboratory. We measured the magnetic torque of the current-generated magnetic moment devices, as well as single-crystalline high temperature superconductors based on iron-pnictide and copper-oxide in a short-interval 65 T magnet. The magnetic torque is found to be linear with magnetic fields for the constant current-generated magnetic moment on the cantilever, which provides validity for our experimental techniques. Furthermore, our measurements clearly resolved the magnetic hysteresis in the superconducting state. In the future, we aim to extend the measurement to higher temperatures in order to study the fluctuation diamagnetism under intense magnetic fields.

Emergent Phenomena in Quantum Hall Systems Far From Equilibrium

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Funding:	$0.00 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

The main goal of this project is to study the emergent behaviors of high mobility two-dimensional electron systems (2DES) formed in semiconductor nanostructures which are driven away from equilibrium by dc and/or microwave electric fields. 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. In contrast to the majority of past research efforts, this project is aimed to explore nonlinear phenomena in the regime of separated Landau levels. The long-term goal of the project is to extend our knowledge of noniquilibrium quantum transport to the regime of Shubnikov-de Haas oscillations and, eventually, to the quantum Hall effect regimes. In particular, the project will explore the feasibility of realizing related nonequilibrium phenomena for composite fermions.

FY 2012 HIGHLIGHTS

(1) We studied a waveform of microwave-induced resistance oscillations over a wide range of microwave frequencies and magnetic fields, covering the regimes of both overlapping and separated Landau levels. Surprisingly, we found no appreciable change in the waveform upon crossing over to separated Landau levels. These findings present significant challenge to existing theories.

(2) We discovered an unusually strong and sharp photoresistance peak due to magneto-plasmon resonance in the regime of separated Landau levels. Tuning the microwave frequency allowed us to superimpose this peak onto a zero-resistance state, without completely destroying it, and to extract theoretically predicted underlying absolute negative resistance.

(3) We studied Shubnikov-de Haas oscillations at very high in-plane magnetic fields. We found that the spin and cyclotron splittings become equal over a wide, continuous range of tilt angles, but only near certain, angle-dependent filling factors. At high enough angles, we observed a beating pattern indicating multiple level crossings, all occurring at the same angle. We explained these findings by finite thickness effects which, with an in-plane magnetic field, give rise to the increase of the effective mass.

(4) We investigated nonlinear magnetotransport in 2DES subject to weak electric fields over a wide range of magnetic fields. At low field, the differential resistivity acquires a correction which increases exponentially with the magnetic field. At higher magnetic fields, however, the correction becomes independent on the magnetic field which marks a crossover into the regime of separated Landau levels. It remains to be seen if these results can be used to extract the Landau level width and shape.

Tunneling and Transport in Nanowires

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Funding:	$150,000

PROGRAM SCOPE

Our goal has been 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 structures prepared using *physical* rather than chemical or biological techniques. The focus is on the investigation of properties of nanowires that are either quasi-one-dimensional (quasi-1D) or one-dimensional (1D). When the transverse dimensions of a wire are smaller than the inelastic scattering, phase coherence, or superconducting coherence lengths, the wires are quasi-1D. One-dimensional wires are those for which the transverse dimensions are smaller than the Fermi wavelength and only the longitudinal electronic degree of freedom is relevant. For such 1D wires, Landau's Fermi liquid theory fails and is replaced by Tomonaga-Luttinger Liquid (TLL) theory. We propose to carry out two types of experiments on nanowires prepared using electron beam lithography (EBL). The first type involves studies of quasi-1D superconducting nanowires. Such superconducting nanowires may have technological significance, as they may provide a path to superconducting q-bits that does not rely on oxide barrier Josephson junctions. The second type of experiment will be directed at exploring the TLL regime of a 1D wire, prepared from a low carrier density material, electrostatically doped $SrTiO_3$ and $KTaO_3$.

FY 2012 HIGHLIGHTS

In a search for h/e flux quantization in ultra-small superconducting rings, we discovered a surprisingly high resistive state, which turns on at the superconducting transition. This appears to be an interface effect that precludes studying h/e quantization in such rings. A manuscript describing these results has been submitted for publication. We are progressing in our efforts to determine the mechanism for the restoration of superconductivity of quasi-1D nanowires driven resistive by current that occurs upon the application of magnetic field. We have conjectured that this effect involves a coupling to dissipation provided by quasiparticles generated in the superconducting electrodes, whose density is enhanced by the application of a magnetic field. To check this hypothesis we have been preparing samples in which a nanowire is coupled to a tunable source of dissipation, a two-dimensional electron gas (2DEG) whose conductivity is tunable. We have also been developing the technology needed to produce nanowires by electrostatic doping of EBL patterned crystals of $SrTiO_3$ or $KTaO_3$. If the wires can be made sufficiently narrow, then they should exhibit TLL behavior, which can be ascertained by studying charge transport. By employing electrostatic gating, we should be able to tune between the 1D and quasi-1D regimes so as to determine the phase diagram as a function of carrier concentration.

NRC's Condensed Matter and Materials Research Committee

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Funding:	$64,000

PROGRAM SCOPE

This project provides partial support for the National Research Council's (NRC) Condensed Matter and Materials Research Committee (CMMRC). The CMMRC is a multidisciplinary group with membership drawn from universities, industry, and government laboratories. The areas of expertise represented on the committee are intended to cover the breadth of the condensed matter and materials research fields. Nominees for committee membership have been and will continue to be selected on the basis of demonstrated intellectual leadership in these areas and thoughtful consideration of cross-cutting issues. The operating guidelines of CMMRC include the following objectives: (1) to respond to requests for technical information and assistance, both from within the National Academies and from outside federal research agencies; (2) to initiate and oversee ad hoc studies in these fields and their multidisciplinary connections to other fields of science and technology; (3) to serve as long-term stewards for studies initiated under CMMRC's direction; (4) to act as an educational resource for the condensed matter and materials research communities and the agencies that support them; and (5) to provide a forum for discussion among condensed matter and materials scientists and Washington D.C. policymakers. To carry out those objectives, CMMRC meets on an annual basis and between those meetings, conducts its business through telephone conferences.

FY 2012 HIGHLIGHTS

CMMRC conducted two face-to-face meetings and conducted the rest of its business via teleconferences and emails. At its fall 2011 meeting, held on November 4-5, 2011 at the Beckman Center in Irvine, California, the committee held a focus session on how to effectively communicate about research to the general public and spent much of the rest of the meeting developing a brief report that describes recent areas where materials research has produced significant benefits for society. The main focus of its spring 2012 meeting, held on May 7-8, 2012 at the Keck Center in Washington, DC, was a series of talks on recent developments in the areas of self-assembly, functionality, and complexity. It also heard from and engaged in discussions with representatives of the agencies that support materials and condensed matter research.

Fundamental Studies of High-Anisotropy Nanomagnets

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Funding:	$115,000

PROGRAM SCOPE

This project is focused on a key class of materials important in magnetism and nanoscience. The specific target is nanometer-length-scale and real-structure control of structures as a means of creating nanomaterials with high magnetic anisotropy and high coercivity. Innovative aspects of the research include synthesis of new magnetic nanostructures with special fabrication techniques. The research consists of three main parts. The first is aimed at preparation and properties of nanoscale clusters and particles where anisotropic structures and surface effects are expected to lead to new high-anisotropy nanomagnets. Both rare-earth-free and rare-earth-containing Co-Fe-rich systems are explored. The second part is focused on new thin-film nanomagnets and unconventional alloy structures. Here, the goals are to control the coercivity and anisotropy in hexagonal and related structures, where exchange and anisotropy effects of substitutional and interstitial doping are investigated. The third part is aimed at understanding the effects of spatial confinement on magnetic hardening in nanoscale structures undergoing structural transformations. This topic is highly important in magnetic nanomaterials since many of them have to be thermally processed to create nanophases with desired hard magnetic properties.

FY 2012 HIGHLIGHTS

We have made progress in several areas of magnetism of high-anisotropy nanomagnets. We have been able to produce and study nanoclusters of $SmCo_5$, YCo_5, Co(Hf), Co(Zr), $HfCo_7$, and others. The anisotropy of these clusters, of size less than 10 nm, generally is similar to but somewhat less than bulk materials. This can be understood on the basis of surface effects. Coercivity values of order 10 kOe have been measured. New work has shown our ability to align the easy axes of single-crystal nanoclusters *before* assembly in a single-phase or two-phase nanocomposite. This work provides a pathway for high-energy magnetic materials. A second area of emphasis is the template-assisted growth of aligned $L1_0$-structure FePt and FePt:Fe_3Pt nanocomposites. Very large coercivities, up to about 50 kOe, have been observed along with energy products of order 60 MGOe. The effects of exchange coupling between grains has been clearly demonstrated. Finally, we have written two invited reviews on prospects for nanoparticle-based permanent magnets and assembly of magnetic nano-objects.

Experimental Study of Magnetic Correlation and Induced Superconductivity in Graphene Crystals

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Funding:	$160,000

PROGRAM SCOPE

Graphene, a two-dimensional crystal consisting of a single atomic plane of carbon, can give access to extraordinary electronic properties reflecting charge carriers that mimic ultra-relativistic elementary particles. Beyond providing a platform that can extend the range and scope of the core capabilities in the electronic and computer industries, these crystals constitute a vast playing field for unconventional physical phenomena. The research explores the emergence of new physical phenomena and the feasibility of devices based on the unique charge carriers in graphene. It addresses basic questions about the properties of graphene and about the nature of its charge carriers: *What is the role of interactions? Can one observe new phases in a magnetic field including fractional quantum Hall effect and broken symmetry phases? What is the interplay between massless Dirac fermions and Copper pairs at the boundary between graphene and a superconductor?* The experiments will be carried out on graphene samples that are minimally disturbed by substrates. We will study either suspended samples (from leads or as a membrane) or decoupled graphene on conducting substrates and will employ a combination of scanning tunneling microscopy and spectroscopy, atomic force microscopy, and magneto- transport.

FY 2012 HIGHLIGHTS

We devised non-invasive experimental probes which allowed us to access the intrinsic electronic properties of graphene. These methods include the fabrication of suspended graphene devices and the use of minimally invasive substrates such as graphite, chemically modified insulators, and a second layer of graphene. Our local probes included scanning tunneling spectroscopy and microscopy (STM/STS), and minimally invasive probes for transport measurements. We demonstrated that it is possible to decouple a graphene sample from substrate induced perturbations not only by suspending it but also by employing non-intrusive substrates such as graphite chlorinated SiO_2 and a second layer of graphene. We used STM/STS to measure the intrinsic density of states of graphene, the anomalous sequence of Landau levels, effects of electron-electron and electron-phonon interactions, and to quantify coupling to the substrate. For two-layer graphene samples, we discovered an unexpected dependence of the electronic properties on the relative orientation of the layers. Orientations that twisted away from Bernal stacking led to qualitative changes in the band structure which were sensitive to the twist angle. Other results include the observation of a correlation-induced enhancement of the Fermi velocity near the Dirac point, spatial mapping of the electronic wave function, and its evolution with the filling of Landau levels.

Raman Spectroscopy of Iron Oxypnictide Superconductors

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Funding:	$140,000

PROGRAM SCOPE

The objectives of this project are to (1) investigate the manner in which charge, spin and lattice coupling, and dynamics evolve through various low-temperature and doping-concentration phases of iron oxypnictide superconductor materials by employing low-frequency electronic Raman (i.e., inelastic light scattering) spectroscopy and (2) clarify the microscopic origin of unconventional superconductivity and magnetism in these compounds. Among the anticipated outcomes of this project are (1) elucidation of the microscopic origin of superconductivity in the iron-pnictide family of materials, (2) insights into how to design new materials with enhanced superconducting properties, and (3) determination of a complete spectrum of collective excitation for the new family of unconventional multi-band superconductors driven by magnetic interactions.

FY 2012 HIGHLIGHTS

We have completed spectroscopic infrastructure development and installation for light scattering studies of pnictide superconductors; established collaboration with the world best materials groups producing single crystals from multiple families of the iron oxypnictide superconductors; developed a new technology to handle, control, and measure sub-millimeter sized single crystals in controlled environment and at low temperatures; and performed series of polarized low-temperature Raman scattering studies of phononic, electronic, inter-band, and magnetic excitations on the several families of the oxypnictide compounds. The results were disseminated at the APS March meetings and several international conferences. Our recent publication [Phys. Rev. B 86, 134107 (2012)] that is reporting on the role of precursor phase transitions for the iron-chalcogenide superconductor $K_{0.75}Fe_{1.75}Se_2$ with superconducting transition at about 30 K received the Editors' suggestion icon.

Coexistence of Superconductivity and Magnetic Order in $RuSr_2GdCu_2O_8$ probed by ^{99}Ru and ^{57}Fe Mössbauer Effects

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Funding:	$130,000

PROGRAM SCOPE

The overall goal of the project was to investigate coexistence in magnetic and superconducting compounds by the Mossbauer Effects of ^{57}Fe and ^{99}Ru.

FY 2012 HIGHLIGHTS

Sr_2YRuO_6 is antiferromagnetic below 26 K and has been shown to super-conduct at 45 K when doped with a few percent Cu. The pure compound has been measured by ^{99}Ru Mossbauer Effect(ME) spectroscopy to investigate multiple phase transitions at 26 and 32 K, found by R. P. Singh and C. V. Tomy [*Phys. Rev. B* 78, 024432 (2008)]. ^{99}Ru ME measurements do not observe the transition at 32 K found by Singh et al. nor the more the recent neutron results by Granado et al. (unpublished). It is found that fluctuations start at 26 K and persist to 28 K but are gone by 30 K, so no static magnetic field is seen beyond 28 K by ME spectroscopy. The fluctuations are too fast to be observed by the 20 ns half-life of the Mossbauer state in ^{99}Ru. This work is presently in review in *Phy. Rev. B*.

$GdSr_2RuCu_2O_8$ is antiferromagnetic below 130 K and is a superconductor below 30 K (depending on preparation). The Cu site has no measured hyperfine magnetic field below the superconducting transition, while the Ru site has 60T hyperfine magnetic field at 4.2 K. This compound has been doped with ^{57}Fe to investigate the Cu and Ru sites. Interestingly, we have found a transition at about 35 K where half the ^{57}Fe nuclei lose their magnetism. It is very possible that those sites which lose their magnetism are Cu sites and the other sites may be Ru sites. No such transition occurs at the Ru sites in the pure compound. It is uncertain in the pure compound how superconductivity, which is thought to exist in the CuO planes, connects across magnetic RuO planes. And it is intriguing that this transition at 35 K occurs near the same temperature as the superconducting transition temperature of nearly 40 K.These are questions to be answered by further ME measurements as a function of temperature and external magnetic field measurements.

Quantum Coherence and its Manipulation in Coupled Quantum Dots

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Funding:	$163,000

PROGRAM SCOPE

There has long been great interest in the modifications to material properties that arise when charge carriers are confined in nanostructures, such as nanotubes, nanowires, and quantum dots. The strong many-body interactions characteristic of these structures, and the interplay of these interactions with quantum size effects, can lead to the formation of novel correlated states of matter, not normally associated with their bulk counterparts. In this research, we provide a specific illustration of these ideas, by focusing on the consequences of many-body interactions for electron transport in the quasi-one-dimensional conductors known as quantum point contacts (QPCs). It has been widely suggested that the interplay of quantum confinement and carrier-carrier interactions can give rise to an unusual spin polarization in these structures.

In our currently-funded DoE research, we have provided strong evidence that this behavior is related to the formation of a self-consistent bound state near pinch-off, which essentially allows the QPC to serve as a natural, single-electron trap. While this idea is certainly exciting, there are a number of important questions regarding the microscopic character of the self-consistently formed bound state that remain unresolved. These include the characteristics "storage time" of electrons on the bound state, the manner in which the bound state forms as the QPC is tuned from open conduction to pinch-off, and the spin-dependent structure of the bound state. To address these issues, this work develops new experimental techniques to probe the microscopic properties of the bound states in QPCs, thereby revealing the fundamental processes that give rise to their formation. A major direction for our research involves the development of transient-measurement schemes, as a means to investigate the localization of single electrons on QPC bound states, and to probe the details of their spin dynamics. In parallel with this, we also investigate the application of QPCs as an "on-demand" source of quantum states that can be used to implement sophisticated systems, in which spatially-remote quantum states interact with each other via a common continuum. Resolving these questions addresses key fundamental issues in condensed matter physics while offering new approaches to quantum control of charge carrier.

Thermodynamics of Strongly Correlated Fermi Gases

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Funding:	$220,000

PROGRAM SCOPE

The purpose of the proposed program is the broad study of the thermodynamic properties of a strongly correlated Fermi gas of ^{6}Li atoms. The primary goals are to (1) 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) 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 2012 HIGHLIGHTS

We moved the JETLAB group from Duke University to North Carolina State University. We published two important papers. The first is the theory of a new dark-molecular state method for optical control of interactions, supported in part by AFOSR, which has a synergistic relation with the DOE program. The second is observation of polaron-to-polaron transitions in the radio-frequency spectrum of a quasi-two-dimensional Fermi gas, supported in part by ARO. The results suggest that the ground state may be approximated by a gas of non-interacting polarons. A new imaging system for these experiments is now in place and will permit thermodynamic studies in two-dimensions. We plan to control dispersion and explore tunable interactions in this system for both 1- and 2-dimensional confinement.

Antiferromagnetism and Superconductivity

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Funding: $150,000

PROGRAM SCOPE

There are many exciting manifestations of the interplay between magnetism and superconductivity that will influence theoretical and experimental work in the next few decades. These developments originate in basic scientific understanding and thereafter spread through our knowledge base to affect engineering and applications that have impact on our society. There are two components to this impact: (1) the education and training of personnel who can knowledgably participate in the process and (2) scientific discovery. We are studying vortex structures in cuprates, specifically to investigate our first report in *Nature Physics* of electrical charge trapped on the vortex core. This discovery points to a mechanism that can seriously alter the stability of vortex structures and that is so important in applications of superconductivity in magnetic fields. We are studying the doping sensitivity of magnetism in the vortex cores in Bi2Sr2CaCu2O8+d, carried to very high magnetic fields. Secondly, we are investigating the vortex dynamics in the new class of pnictide superconductors using a sensitive, microscopic-based tool, NMR spin-spin and spin-lattice relaxation. Thirdly, we are growing and characterizing the highest quality of UPt3 single crystals ever produced to investigate competing orders for magnetism and superconductivity in this system to determine the order parameter symmetry and vortex structures in UPt3 and the coupling of its magnetism to superconductivity. The experimental work will involve nuclear magnetic resonance studies at Northwestern University as well as at the National High Magnetic Field Laboratory. In summary, we are performing neutron scattering investigations of vortex structures using national facilities, phase sensitive determinations of superconducting order symmetry, and tests of broken-time reversal symmetry.

FY 2012 HIGHLIGHTS

We have new results from the past year, presented at international meetings, that elucidate the pseudogap phase of unusually high quality cuprate single crystals of Hg1201 from Martin Greven's group. The pseudogap does not appear robustly off plane, and our results are inconsistent with theoretical models of loop currents proposed by Chandra Varma as interpreted by Steve Kivelson. Our new results on the vortex state in an iron-pnictide electron-doped superconductor NaFeCoAs are from the highest quality optimally doped crystals in the literature and are provided by Pengcheng Dai. In the past year, we have used neutron scattering to measure the *bulk* susceptibility of superconducting UPt3 crystals of the highest possible quality produced in our world class crystal growth facility. The results show unambiguously that the superconducting state in the B-phase is an equal spin-pairing state. Future work will confirm the precise nature of this triplet state and if in fact it is a chiral state. This work has appeared in the *Physical Review B*.

Experimental Study of Superconductivity in Reduced Dimensions and in Novel Materials

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Funding: $135,000

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 and pursue a suite of electron transport measurements including superfluid density, resistivity, and Hall coefficient. Quantum fluctuation effects are expected in the magnitude and temperature dependence of the superfluid density as well as the high-field Hall effect.

FY 2012 HIGHLIGHTS

(1) We grew smooth homogeneous thin films of the very-anisotropic superconducting compound Bi2Sr2CaCu2O8+x (Bi-2212). Previously, we had grown homogeneous films, but they had rough surfaces. Measurements of the superfluid density λ-2(T=0) in the smooth films showed that the quantum scaling of transition temperature, Tc, with λ-2(0) in Bi is in quantitative as well as qualitative agreement with similar measurements on two-dimensional films of the cuprate YBa2Cu3O7-δ. Measurements of the resistance of the Bi-2212 films shows that there is a significant temperature interval between the temperature where resistivity seems to vanish and the temperature where superfluid density turns on, consistent with a wide regime of two-dimensional thermal fluctuations.

(2) We have made significant progress in developing our novel technique for determining the superconducting coherence length, ξ, in superconducting films. 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. We have shown that the technique works for a-MoGe films, for which we can determine ξ by alternate methods. We will test on other materials, e.g., Nb, then apply to thin cuprate films. We have submitted to *Physical Review B* a theoretical paper on the thermodynamic lower critical field for vortex generation in 2D superconducting films.

Optical Study of Spin Dynamics in Semiconductor Nanowires

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Funding:	$220,000

A summary for this program was not available at press time.

Investigation and Manipulation of Nanoscale Molecular Superconductivity

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Funding:	$135,000

PROGRAM SCOPE

We propose to perform atomic-level investigations of *nanoscale* superconductors formed by charge transfer molecular systems on metallic surfaces using scanning tunneling microscopy and atomic/molecular manipulation. We plan to advance the molecular superconductivity research in two critical areas: (1) fundamental properties and (2) manipulation of charge states of molecular superconductors. In the first part, we will measure superconducting gaps, explore superconductor-metal phase transitions, and investigate proximity effect at superconductor-metal boundary. In the second part, we will manipulate the charge state of the molecular superconductors by adding additional donor and acceptor molecules locally. The effect of substrate electron confinement on the superconductivity will also be studied using hybrid cluster-quantum corral devices. Our project includes both conventional and innovative components, and the achievements will impact fundamental understanding of nanoscale superconductivity and its potential applications in energy sciences.

FY 2012 HIGHLIGHTS

We have found a new molecular self-organization on Ag(111) that shows superconducting gap. Unlike previous findings, where two layers of BETS molecules form the nanoscale superconducting clusters, only one layer of BETS is assembled with the $GaCl_4$ molecules. This molecular assembly satisfies the required stociometric ratio of 2 BETS for every $GaCl_4$; a necessary condition for superconducting in this type of system. Although the molecule-surface intereaction should be enhanced in this case, we still find a clear superconducting gap. We have also completed the study of superconductor-metal boundary and molecule-metal interfacial effects. Here, tunneling spectra reveal the quenching of the free surface state electrons of Ag(111) at 2 nm distance from the superconductor-metal boundary while theoretical calculations confirmed a charge transfer from the BETS to $GaCl_4$ on Ag(111) resulting in a metallic state. Both are critical findings to understand the superconducting phenomena observed in nanoscale moelcular clusters.

We are also investigating an organic-organic hybrid superconductor-magnetic system composed of a molecular superconductor and a magnetic molecular motor. For this, a stand-alone molecular motor having multiple components—a tripod stator, a five-arm rotor with magnetic atoms, and an atomic ball bearing—is used. By means of inelastic electron tunneling, selective excitations of different molecular parts have be realized, and the electron energy transfer induces mechanical motions of the motor. Strikingly, we discover that selective tunneling into a specific rotor arm results in a controlled directional rotation of the motor; thereby a controlled energy transduction at the nanoscale has been achieved.

Spin-Polarized Scanning Tunneling Microscopy Studies of Nanoscale Magnetic and Spintronic Nitride Systems

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Funding:	$80,000

PROGRAM SCOPE

This DOE-sponsored project has two important goals: (1) probe the fundamental electronic and magnetic properties of technologically-promising bilayer systems consisting of an atomic layer of magnetic material on top of a layer of nitride semiconductor material, and (2) firmly establish a strong U.S.-led research effort in the field of spin-polarized scanning tunneling microscopy (SP-STM). In the project, magnetic/spintronic nitride bilayer systems are synthesized using the technique of molecular beam epitaxy and/or pulsed laser epitaxy, in which the properties of the growing surface are carefully tailored by monitoring the process via in-situ reflection high energy electron diffraction. Using this method, it is possible to create magnetic nitride layers of all types—ferromagnetic, antiferromagnetic, and spintronic layers involving dilute magnetic doping. Another important aspect of the project looks at correlated properties, including correlations between nanometer scale surface structure and the electronic and magnetic properties.

In fulfilling the second objective, PI Smith draws upon a decade of experience in the field of SP-STM. In this technique, a sharp needle-like, metallic probe with an ultra-thin magnetic coating is brought to within a few atomic diameters away from the sample surface of interest. As the tip scans across the surface, the tunneling current between tip and sample responds to minute changes in the magnetic conductance of the tip-sample junction. These minute variations then yield a two-dimensional mapping of the magnetic spin structure of the surface. Application of a magnetic field during this process provides additional information by polarizing either the tip or sample magnetization, thus enabling both in-plane and out-of-plane sensitivity.

FY 2012 HIGHLIGHTS

The PI’s group has made several key accomplishments relating directly to the two main stated objectives. First of all, one paper published in *Applied Physics Letters* details the discovery of quantum height MnGa islands formed via a spontaneous process on gallium nitride surfaces. The next step is to determine the detailed crystalline structure and magnetic properties of these islands. Second, a paper has been published in *Nano Letters* which details the discovery of an unexpected orthogonal magnetic anisotropy occurring on the stepped surfaces of manganese nitride spin pyramids; in this study, the power of SP-STM was fully utilized in order to map out the novel magnetic ordering. And thirdly, in a paper published in *Journal of Applied Physics*, a unique method has been demonstrated for embedding an atomic layer of manganese atoms in a gallium nitride thin film, which may lead to the possibility of magnetic delta-doped, spintronic gallium nitride.

Engineering of Mixed Pairing and Non-Abelian Majorana States of Matter in Chiral p-Wave Superconductivity in Sr_2RuO_4 and Other Materials

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Funding:	$130,000

PROGRAM SCOPE

The goal of the proposed research is to seek out novel quantum states of matter in chiral *p*-wave superconductor Sr_2RuO_4 and related Ru-Sr_2RuO_4 eutectic phase, especially mixed pairing states and non-Abelian Majorana anyons. Initial evidence for half-integer flux quanta has been found in Sr_2RuO_4. However, half-flux Abrikosov vortices, domains, and domain walls expected in a chiral *p*-wave superconductor have been observed in this material. We propose to engineer material and device systems on Sr_2RuO_4 to create experimental conditions that will allow direct observation of mixed pairing and non-Abelian Majorana states of matter. Specifically, we will (1) prepare and characterize superconducting thin flakes of Sr_2RuO_4; (2) perform tunneling as well as electrical transport measurements on Ru-Sr_2RuO_4 eutectic and pure Sr_2RuO_4 to detect mixed pairing states; (3) perform phase-sensitive measurements on Sr_2RuO_4 to control the presence of domains and domain walls, and detect the presence of chiral edge currents; and (4) search for the existence of half-flux-quantum vortices and the associated non-Abelian Majorana anyons.

FY 2012 HIGHLIGHTS

Recently a team at University of Illinois carried out cantilever magnetometry measurements on Sr_2RuO_4 and found evidence for a half-integer-flux-quantum state (J. Jang *et al*., Science, 331, 186 (2011)). To provide an independent confirmation of the existence of such an exotic state and pave the way for the demonstration of the existence of half-flux-quantum Abrikosov vortices, we pursued electrical transport measurements of resistance oscillations in superconducting rings of Sr_2RuO_4 fabricated on mechanically exfoliated single crystals of Sr_2RuO_4 by photolithography and focused ion beam. With the application of a perpendicular field, we observed resistance oscillations with an amplitude much larger than that expected from the conventional Little-Parks resistance oscillations. However, the expected half-integer-flux-quantum resistance oscillations were not found without the application of an in-plane field that is present in the University of Illinois experiment. Similar experiments with the in-plane field is currently underway.

On the other hand, bulk Sr_2RuO_4 has been found to feature vortex lattices at unexpectedly low fields. We have also investigated the consequences of these vortex states on the low-temperature magnetoresistive behavior of mesoscopic samples of Sr_2RuO_4. The pronounced quantum oscillations with a conventional period of the full-flux quantum with the unexpectedly large amplitude and the number of oscillations in thin-wall rings are attributed to vortex-flow-dominated magnetoresistance oscillations rather than a conventional Little-Parks effect. For rings with a thick wall, we found quantum oscillations with two distinct periods in high and low field regimes, respectively, which we argue to be associated with the “lock-in" of a vortex lattice in these thick-wall rings of this exotic superconductor.

Exploration of Artificial Frustrated Magnets

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Funding:	$291,000

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. 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. 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. We are investigating a range of frustrated lattice geometries, thus accessing a range of different types of frustration. We are also examining how these systems respond to disorder and the effects of both static and dynamic external magnetic fields.

FY 2012 HIGHLIGHTS

Magneto-optical Kerr effect studies of square artificial spin ice: We have performed a magneto-optical Kerr effect study of the collective magnetic response of artificial square spin ice. We find that the anisotropic inter-island interactions lead to a non-monotonic angular dependence of the array coercive field, and comparisons with micromagnetic simulations indicate that the two perpendicular sublattices exhibit distinct responses to changing magnetic field that drive the magnetization reversal process. Furthermore, such comparisons demonstrate that island shape disorder plays a hitherto unrecognized but essential role in the collective behavior of these systems. This study led to a paper published in *Physical Review B Rapid Communications*.

Artificial frustrated magnets formed from perpendicular anisotropy materials: While artificial frustrated magnets have previously always been formed from materials with in-plane moments, we have initiated studies of systems composed of circular islands of perpendicular anisotropy materials. These systems have the advantage that the inter-island interactions are isotropic, and that they thus are more amendable to simple theoretical models. The kagome array has qualitatively different magnetostatics but identical lattice topology to previously-studied ‘artificial spin ice’ systems composed of in-plane moments. The two systems show striking similarities in the development of moment pair correlations, demonstrating a universality in artificial spin ice behavior independent of specific realization in a particular material system. A paper based on this research has been published in *Physical Review Letters*.

Studies of Multiband and Topological Superconductors

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Funding:	$130,000

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 shown 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 2012 HIGHLIGHTS

We have observed, for the first time, 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. Scattering, either in the films or the junction barrier, will smear out the features and make each band a single gap value. We have also succeeded in making electrical contacts on a single Bi_2Te_3 nanotube using focused ion beam and characterized the quasi one dimensional properties of the nanotubes.

Long-Range Transport of Excitons in GaAs Coupled Quantum Well Structures

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Funding:	$40,000

PROGRAM SCOPE

This project has had the long-range goal of establishing Bose-Einstein condensation (BEC) of spatially indirect excitons in coupled quantum wells. One investigator at another institution, Leonid Butov at UCSD, has claimed success at seeing BEC of excitons in this system, but no other investigators have reproduced this claim and it is highly in doubt in the field. As steps along the way, we have worked carefully and successfully to establish the trapping of spatially indirect excitons, thermalization of the excitons in a trap, and measurement of their diffusion constant and interactions. These results have been compared to theory developed by the top-notch theory group of Peter Littlewood, his former student Jonathan Keeling, Boris Laikhtman, and Roland Zimmermann (now retired).

Our conclusion thus far is that in the standard experiments like those of Butov, the excitons are too strongly interacting for appearance of a standard BEC and one should expect at most a few percent condensate, similar to liquid helium. The system, however, is a good example of a strongly interacting two-dimensional Bose gas; and transport experiments may see superfluid behavior even where spectroscopic measurements do not for a gas with a very small condensate fraction.

We have found several quite interesting effects which are unrelated to BEC. One is the appearance of rings of luminescence due to recombination at the interface of a 2D hole gas and a 2D electron gas. Another is a linear luminescence up-conversion process in superlattices. A third is the appearance of a dark spot in the center of a trapped exciton gas. This last case has been the topic of much study, as some theorists have claimed that this arises from BEC of excitons in dark states. We have shown that this effect is not due to any enhanced loss process of excitons and is related to the light-hole/heavy-hole crossover when stress is used to shift the exciton bands in the quantum wells.

FY 2012 HIGHLIGHTS

In the past year, we have had two main thrusts. The first has been to study the exciton dark-spot effect using in-plane magnetic field to make the dark excitons slightly allowed to photoluminescence. Our preliminary results are that the magnetic field makes the dark spot become even larger.

Our second thrust has been to make direct electrical contact with the samples in order to do transport experiments which could confirm the superfluid nature of an exciton condensate. The processing has been finished for this set of experiments, and experiments are under way to determine the transport properties.

Magneto-Transport in GaAs Two-Dimensional Hole Systems

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Funding:	$175,000

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 the clean 2D systems has been performed on 2D *electrons* confined to a remotely-doped GaAs quantum well. The goal of this 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 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 which are grown via state-of-the-art molecular beam epitaxy. We use low-temperature magneto-transport measurements to explore their novel physics. Among the problems to be addressed 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 $\nu = ½$, in 2D hole systems confined to wide GaAs quantum wells.

FY 2012 HIGHLIGHTS

We measured the effective mass and spin-susceptibility of a dilute, interacting 2D hole system. We concluded that both of these parameters are slightly enhanced over the band values but the enhancements are much less than what would be expected in a very dilute 2D system where interaction should be dominating. While a satisfactory theoretical explanation for this surprising observation is still missing, it is apparent that the holes' stronger spin-orbit interaction and their j = 3/2 effective spin significantly alter the impact of hole-hole interaction in comparison with the more commonly studied spin j = 1/2 electrons. In a separate set of experiments, we probed the energy band structure of 2D holes through measurements of the Fermi contours when the 2D hole system is subjected to a strong parallel magnetic field. We found a severe distortion of the Fermi contours. Surprisingly, the distortion is spin-dependent and is much stronger for the majority-spin subband.

Probing Correlated Superconductors and their Phase Transitions on the Nanometer Scale

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Funding:	$100,000

PROGRAM SCOPE

This program will focus on understanding how correlated electronic states in materials with d and f electrons undergo phase transitions to form an unconventional metallic phase and the mechanisms by which these states become superconducting states with lower temperatures. Our aim is to provide a microscopic view of these exotic materials and their phase transition into the superconducting state by using scanning tunneling microscopy (STM) and spectroscopy techniques. These experiments will provide important evidence that will help constrain theoretical models of unusual normal states in these complex materials and their potential mechanisms for superconductivity.

This program will be divided into two parts. The first will focus on examining the properties of high-Tc cuprate superconductors and the high-temperature pseudogap phase of these materials. The second component will be to utilize STM techniques to study the exotic normal and superconducting phases in heavy fermion compounds. The parallels between the puzzles in heavy fermions and cuprates suggest that heavy fermions might provide important clues into understanding correlated electrons and their superconductivity. Similar to the high-temperature superconducting cuprates, understanding the mechanism behind the unconventional superconductivity requires understanding the “normal state” prior to formation of superconductivity. The heavy fermions offer clean materials systems to examine issues that might be difficult to explore in the cuprates and new Fe-based superconductors due to doping disorder in those systems. In particular, the issue of proximity to a quantum critical point and the impact of quantum phase transition on the electronic properties of material and mechanism of superconductivity can be precisely probed in heavy fermion systems. The two components of the proposed program provide a broad attack on some of the most important problems in the physics of correlated materials and the emergence of superconductivity in these systems. Finally, the program will support the development of spin polarized STM measurements of correlated systems that can complement other STM measurements to directly probe the spin textures in such systems.

FY 2012 HIGHLIGHTS

We made an exciting advance in the study of heavy fermion compounds by using spectroscopic mapping with the scanning tunneling microscope to detect the emergence of heavy excitations upon lowering the temperature in a prototypical family of Ce-based heavy fermion compounds, (Nature 2012). Additionally, we constructed a spin-polarized STM capable of performing spin resolved experiments on correlated materials. We were able to prepare clean metal samples in situ and obtained the first STM images with this machine at 1.2K. In the coming months, we will install evaporators for in situ preparation of magnetic atoms, so as to prepare spin-polarized tips, and to perform the first spin-polarized STM experiments.

Transport Experiments on 2D Correlated Electron Physics in Semiconductors

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Funding: $165,000

PROGRAM SCOPE

The goal of this project is to design and carry out experiments on two-dimensional electron systems in advanced semiconductor heterostructures to probe into previously inaccessible physical regimes to explore deep into the fundamental physics of the fractional quantum Hall effect. In these experiments, transport and magnetotransplant measurements will be made at low temperatures in the milli-Kelvin and sub-milli-Kelvin ranges, using dilution refrigerators in Sandia National Laboratories and the nuclear demagnetization refrigerators in the High B/T Facility of the National High Magnetic Field Laboratory. In case of the experiments designed for the sub-milli-Kelvin temperature measurements, using the nuclear demagnetization refrigerator, special cooling stages and a hydrostatically operated tilting platform have been designed, constructed, and successfully tested in one preliminary experiment. Results from these experiments are expected to uncover novel fractional Hall states with unprecedentedly low excitation gaps, and also to elucidate the nature of the quantum phases of previous observed states in the second Landau level.

FY 2012 HIGHLIGHTS

We have carried out tilt magnetic field studies of the $v=12/5$ fractional quantum Hall state, which is believed to be a spin-polarized non-Abelian parafermionic state. The tilt experiment, performed using the hydraulically driven rotator in a nuclear demagnetization refrigerator, shows that the tilt field dependence at $v=12/5$ is strikingly different from that at $v=5/2$, and is inconsistent with theoretical models proposed for it being a spin-polarized state.

Engineering Topological States of Matter and Search for Majorana Fermions

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Funding: $275,000

PROGRAM SCOPE

In the proposed work, we will design a system which supports Majorana excitations and study properties of this new unconventional state of matter. Specifically, we will fabricate one-dimensional semiconductor wires where superconductivity is induced 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.

Non-Abelian statistics of Majorana particles means that some quantum numbers of the mani-particle condensate are protected from small local perturbations. One can use these protected degrees of freedom to encode quantum information. As such, topological quantum computing presents a robust alternative to the conventional quantum computation, where decoherence poses the major technological challenge. From this perspective, the search for Majorana fermions has a practical relevance apart from scientific curiosity and intellectual pursuit of discovery.

FY 2012 HIGHLIGHTS

Over the first month of the project (the project started on September 1, 2012), we concentrated on the optimization of superconductors sputtering. We succeeded in the growth of NbN thin films with Tc=13 Kelvin and critical fields 13.2 Tesla. A larger superconducting gap will afford weaker semiconductor-superconductor coupling in the future devices and, correspondingly, easier electrostatic control of carrier density.

Experiments on Quantum Hall Topological Phases at Ultra-Low Temperatures

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Funding:	$135,000

PROGRAM SCOPE

This project is to cool electrons in semiconductors to extremely low temperatures and to study new states of matter formed by low-dimensional electrons. At such low temperatures (and with an intense magnetic field), electronic behavior differs completely from ordinary ones observed at room temperatures. Studies of electrons at such low temperatures would open the door for fundamental discoveries in condensed matter physics. Present studies have focused on topological phases in the fractional quantum Hall effect. This project consists of the following components: (1) Development of efficient sample cooling techniques and electron thermometry: Our goal is to reach 1 mK electron temperature and reasonable determination of electron temperature. (2) Experiments at ultra-low temperatures: Our goal is to understand the energy scale of competing quantum phases, by measuring the temperature-dependence of transport features. Focus will be placed on such issues as the energy gap of the 5/2 state and those of 12/5 (and possible 13/5), and resistive signature of instability near 1/2 at ultra-low temperatures. (3) Measurement of the 5/2 gaps in the limit of small or large Zeeman energies: Our goal is to gain physics insight of 5/2 state at limiting experimental parameters, especially those properties concerning the spin polarization. (4) Experiments on tuning the electron-electron interaction in a screened quantum Hall system: Our goal is to gain understanding of the formation of paired fractional quantum Hall state as the interaction pseudo-potential is being modified by a nearby screening electron layer.

FY 2012 HIGHLIGHTS

The project has progressed well according to the plan described in the proposal. In particular, we have completed the experiments of the 5/2 fractional quantum Hall state under a small in-plane magnetic field; a paper based on the results from this experiment has been published in a major physics journal, the *Physical Review letters*. Our collaborators in Princeton group have successfully grown high quality double layer carbon-doped 2D hole gas for our experiments on screened fractional quantum Hall effect in ultralow temperatures. We have characterized these wafers and are preparing for systematic measurements using gate-controlled quantum devices.

Nanostructure Studies of Strongly Correlated Materials

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Funding:	$140,000

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 magnetite (Fe_3O_4), vanadium dioxide (VO_2), layered dichalcogenides ($TiSe_2$), and rare earth nicklates (e.g., $NdNiO_3$). All 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 as a gating medium to tune the surface charge density and hence the state of the material) to gain insights into the underlying physics behind the transitions and the relevant ordered states.

FY 2012 HIGHLIGHTS

The main highlight of FY 2012 has been the discovery that atomic hydrogen (produced catalytically through the splitting of H_2 gas by metal electrodes and nanoparticles) can be used to dope VO_2, with dramatic implications for the metal-insulator transition. In single-crystal nanowires, carefully suspended to minimize the perturbing effects of strain, we find that it is possible to eliminate the insulating phase entirely, stabilizing the metallic state (in a distorted form of its crystal structure) down to cryogenic temperatures. This doping is reversible, as the hydrogen may be removed from the material, restoring its original electronic properties and phase transition. This is enabling new studies of this stabilized metallic state to understand the role of electronic correlations. This work was published in Nature Nanotechnology (Nature Nano 7, 357-362 (2012)). We have also found that ionic liquid gating of these nanowires seems to have very little effect beyond what we ascribe to electrochemical doping with hydrogen. This work (Nano Lett. 12, 2988-2992 (2012)) is important, as there is currently an ongoing controversy regarding the efficacy of ionic liquid gating in this material system.

Spectroscopy of Degenerate One-Dimensional Electrons in Carbon Nanotubes

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Funding: $150,000

PROGRAM SCOPE

We are studying 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 terahertz (THz) to 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 2012 HIGHLIGHTS

We have used post-synthesis separation methods based on density gradient ultracentrifugation to produce aqueous suspensions strongly enriched in armchair, or (n,n), carbon nanotubes. Through resonant Raman spectroscopy of the radial breathing mode phonons, we provided macroscopic and unambiguous evidence that density gradient ultracentrifugation can enrich armchair nanotubes. Furthermore, using optical absorption spectroscopy in the near-infrared and visible range, we showed that interband absorption in armchair nanotubes is strongly excitonic. Lastly, by examining the G-band mode in Raman spectra, we determined that observation of the broad, lower frequency (G^-) feature is a result of resonance with non-armchair metallic nanotubes. These findings regarding the fundamental optical absorption and scattering processes in metallic carbon nanotubes lay the foundation for further spectroscopic studies to probe many-body physical phenomena in one dimension.

Optical Spectroscopy of Defects and Dopants in Nanocarbon Materials

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Funding:	$156,000

PROGRAM SCOPE

The objective of this project is to control and understand the influence of defects and dopants on the physical properties of carbon nanotubes and graphene. Carbon nanotubes and graphene are attracting high scientific and technological interest because of their unique physical properties, such as high mobility, thermal conductivity, mechanical robustness, and chemical stability. However, the physical properties of these nanocarbon materials are strongly affected by impurities and structural defects. For example, a conducting graphene sheet turns into a semiconductor when it is cut into a narrow ribbon. Furthermore, its edges give rise to localized states that have a strong influence on transport properties. Thus, the intentional generation of defects and dopants in nanocarbons provides an opportunity to engineer electronic and optical properties, similar to semiconductor device technology.

In this project, near-field Raman spectroscopy is used to zoom-in on single defects and dopants. This method uses a metal tip as an optical antenna to localize and enhance incident laser radiation and to interact locally with nanocarbon materials. The technique makes it possible to measure local electronic and structural properties with a spatial resolution of 10-20 nm and has been used to record high-resolution spatial maps of optically active phonons and localized photoemission. These measurements have been complemented by temperature-dependent studies to relate localized modes to physical parameters, such as the electronic phase-breaking length.

Our continuing work builds on the instrumentation and capabilities established over the past ten years. The goal is to systematically study the symmetry breaking nature of 'model' defects and dopants. Defects are generated by ion bombardment, and the defect density is controlled by the ion dose. Spatial maps of optically active phonons are recorded as a function of temperature and defect density. In order to perform near-field Raman and temperature measurements simultaneously, we are developing a cryogenic near-field Raman instrument. We combine near-field Raman scattering with local electrostatic doping to control the local Fermi energy and to study its influence on exciton recombination and the electron-phonon interaction. We also explore coherent Raman scattering, such as stimulated Raman scattering and coherent anti-Stokes Raman scattering, to boost the signal to noise ratio and increase the sensitivity to local defects.

The ability to zoom-in on single defects and to measure local physical properties provides valuable feedback on the physical properties of carbon nanotubes and graphene ribbons, and provides input for new device concepts and for improved material synthesis.

Transport Behavior of Superconductors at High Dissipation and Short Timescales

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Funding:	$110,000

PROGRAM SCOPE

Many new effects and regimes unfold in superconductors as they are pushed to extreme conditions of electric field, power densities, current densities, and vortex velocities. Besides their own novelty, these phenomena yield fundamental information about the superconducting state and its parameters, as well as its practical limits for technological applications. Furthermore, some of these effects (such as formation of phase slip processes and the acceleration of superfluid) are time-dependent on time scales such as quasiparticle-phonon energy relaxation and gap relaxation. The goal of this project is to use fast low-duty cycle pulsed signals to, first of all, access these regimes without excessive heating and, secondly, to observe directly in the time domain the temporal unfolding of these phenomena on nanosecond time scales. So far this project has led to the discovery of new effects in the transport behavior in superconductors, has provided new information on fundamental parameters, and has helped establish intrinsic strengths and limitations of different superconducting materials for applications.

The primary tool we have developed for extending the range of measurable dissipation densities is to use short-duration pulsed-current and pulsed-voltage sources. This allows us to conduct measurements at power densities in the 10 gigawatts per cubic centimeter range and at electric fields in the kilovolt per centimeter range. We recently developed the ability to simultaneously track current and voltage, and cross correlate them with sub-nanosecond temporal resolution.

FY 2012 HIGHLIGHTS

Two major developments this year were the study and experimental confirmation of two new effects that were theoretically predicted many years ago. One is the regime of thermally activated dynamics of spontaneous edge nucleated vortices. This mechanism was proposed by Gurevich and Vinokur in a Physical Review Letter in 2008. The other result is the experimental elucidation of the vortex explosion transition. This effect was theoretically proposed more than 30 years ago by Likharev in a Modern Physics Letter article in 1979.

Spin Physics Program

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Funding: $122,000

PROGRAM SCOPE

Spin-based electronics holds the potential for logic operations that consume less power than equivalent charge based logic operations. To exploit the energy-saving potential of spin currents, it is essential to be able to control them as we control the flow of charge. Recently it has been recognized theoretically that, through intrinsic spin orbit coupling, it is possible to manipulate spin currents via electric fields. This concept is an extremely important approach to spin control and manipulation, as electric-field control of spin will provide a far easier path to adopt spin-based devices into the mainstream of technology. Our ability to manipulate spin currents over macroscopic length scales depends on a complete microscopic understanding of the relevant spin physics. Our research team will perform experiments and develop theories of coupled spin-charge transport. At UCSB and Sandia CINT, we fabricate and process semiconductor state-of-the-art heterostructures. At LBNL, we use transient grating spectroscopy to fully characterize spin relaxation and propagation dynamics. Finally, these capabilities are combined with a strong theoretical team based at Stanford that will help establish the links between new experimental results and theories of spin transport in the presence of spinorbit coupling. This is part of a project led by SLAC National Accelerator Laboratory.

Spectroscopic Investigations of Novel Electronic and Magnetic Solids

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Funding: $146,000

PROGRAM SCOPE

The goal of this project is to investigate the behavior of novel materials under extreme conditions. As you probably know, the interplay between charge, structure, and magnetism is responsible for the rich physics of oxides and many other systems; and external stimuli like magnetic fields, pressure, chemical substitution, and size can influence the competition between these degrees of freedom. Our Department of Energy-supported program pursues these scientific themes in a variety of ways, combining different types of spectroscopy with appropriate tuning techniques, with the overall goal of establishing connections between the dyamical response of a material and its functionality. We currently focus on three major themes: (1) the optical properties of frustrated, multiferroic, thin film polar, and model oxides; (2) the vibrational properties of multiferroic and archetypal oxides; and (3) charge-structure-function relationships in model nanoscale materials. What brings these efforts together is the interplay between charge, structure, and magnetism and the spectroscopic techniques with which we investigate these phenomena. Findings from this comprehensive experimental program advance theoretical development and energy-related applications.

FY 2012 HIGHLIGHTS

We have a number of accomplishments within this broad scientific area. Examples from the past year include discovery of (1) magnetic field-induced color changes in α-Fe_2O_3, (2) spin-spiral quenching in rare-earth substituted-$BiFeO_3$ where combined ferroelectricity and ferromagnetism exists in a narrow substitutional range, (3) amplified magnetoelastic coupling through the magnetic quantum critical transition in $Mn[N(CN)_2]_2$, and (4) size-dependent changes in chemical bonding, magnetoelastic coupling, and core-shell structure in nanoscale oxides like MnO and $CoFe_2O_4$. Continuing efforts focus on the vibrational properties of ferroelectric domains in multiferroic oxides, band gap analysis of thin film oxides, and giant field-induced color changes in frustrated materials. A broad range of educational, outreach, and service activities also take place under the auspices of this Department of Energy grant, especially in the area of conference organization and service to the National High Magnetic Field Laboratory and the National Synchrotron Light Source.

Emergent Behavior in Magnet-Superconductor Hybrids

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Funding:	$150,000

PROGRAM SCOPE

In this project, we study emergent behavior that appears when two mutually exclusive states of matter, superconductivity and magnetism, are combined at the nanoscale in a unified system. We focus our efforts on fabricating new materials, the ferromagnet-superconductor hybrids (FSH). These novel materials contain arrays of nanomagnets embedded into the superconducting film or placed outside the superconducting film. The inhomogeneous magnetic fields, created by nanostructures, are used to pin vortices in superconducting films. With Tesla range magnetic fields from magnetic nanostructures and width/diameter of nanomagnets comparable with the superconducting film coherence length, we study transport properties of the FSH. These magnetic nanostructures can dramatically increase the critical current at magnetic field strength typical for superconducting cables. This provides a possible new way for application of FSH.

FY 2012 HIGHLIGHTS

We have fabricated novel magnetic nanotubes by electroless deposition of Ni inside the pores of the anodic alumina oxide membrane. We have perfected fabrication of Ni nanowires to produce several-dozen-microns-long single crystal nanowire with only 70 nm in diameter. We have performed systematic studies of transport properties of superconducting films with very large coherence length, covered with arrays of parallel magnetic nanostripes. These stripes strongly influence the critical current anisotropy.

Linear and Nonlinear Optical Properties of Metal Nanocrystal Composites Synthesized by Directed Self-Assembly

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Funding:	$180,000

PROGRAM SCOPE

The scientific themes of this project are (1) fabrication, characterization, and ultrafast, nanoscale optics of active, nonlinear metamaterials; and (2) quasiparticle dynamics—for example, exciton-plasmon and photon-phonon coupling—in plasmonic heterostructures. Aided by finite-difference time-domain and finite-element calculations, we design and fabricate a variety of plasmonic "workbenches" on which we can excite quasiparticles (e.g., excitons, phonons, plasmons) using optical signals, electrical impulses and laser-induced mechanical stresses, and mapped material response down to femtosecond time and nanometer length scales. We employ state-of-the-art nanofabrication techniques (e.g., dual layer electron-beam lithography, pulsed laser deposition, colloid-mask lithographies, quantum-well fabrication, and multiple-target magnetron sputtering) to create these novel heterostructures for experiments in which they as serve as model semiconductor-plasmonic systems.

The complex phenomenology of these structures is studied using coherent and time-resolved second- and third-order nonlinear optical spectroscopies, confocal and near-field optical microscopies, and other scanning-probe techniques. Apart from the inherent signal-to-noise enhancement achievable in lithographically fabricated nanoparticle arrays and structures, ensembles of identical nanoparticles allow us to observe coherent interactions between nanoparticles and nanoparticle ensembles (e.g., heterodimers, trimers, and tetramers). The array experiments also form a natural bridge to single-nanoparticle studies using scanning probe optical techniques. The use of coherent spectroscopies—such as interferometric second-order autocorrelation—makes it possible to access the complete set of information available about coupling of plasmons to photons, phonons and excitons, and the interactions among neighboring plasmonic and dielectric structures.

FY 2012 HIGHLIGHTS

We carried out extensive computer simulations (just published) of the linear and nonlinear response of sub-wavelength scale Archimedean spirals that laid the groundwork for building a harmonic-generation experiment to test (experimentally) the unique properties of these completely asymmetric nanostructures. We also completed and published three studies of exciton-plasmon coupling in multilayer heterostructures comprising luminescent centers in zinc oxide thin films or quantum wells and metal nanoparticles, nanoparticle arrays, and lithographically fabricated nanodisks. These studies break new ground by showing how it is possible to (1) use Purcell-enhanced plasmonic coupling to selectively enhance luminescence from specific defects in the zinc oxide luminescence spectrum, (2) locate specific defects at interfaces in the heterostructure using femtosecond pump-probe spectroscopy, and (3) use zinc oxide quantum wells and aluminum nanoparticle arrays to vary and measure exciton-plasmon coupling from weak- to strong-coupling regimes.

Ultrafast Studies of Hydrogen and Related Defects in Semiconductors and Oxides

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Funding:	$200,000

PROGRAM SCOPE

We have expanded our efforts to gain a deeper understanding of ultrafast laser pulse induced coherent acoustic phonons (strain waves), which serve to transiently modify materials in a spatially and temporally localized manner. This approach enables high-resolution depth dependent materials characterization previously unrealized, as well as the promise of selective alteration and manipulation of materials on ultrafast time scales before lattice thermalization and recombination occur. The combination of localized strain and concurrent excited carriers introduces the possibility of novel effects such as local annealing, bond activation, metastable state transitions, transient far-from-equilibrium characterization, and investigating the influence of defect populations on the opto-electronic properties deep within a material.

FY 2012 HIGHLIGHTS

We have performed coherent acoustic phonon measurements of ion-bombarded GaAs and diamond crystals. Using implants at a variety of fluences and an ion track model in GaAs, we have determined that the spatial extent of the modulation to the optical properties of the lattice extend beyond the implantation-induced structural disorder by an order of magnitude. However, the optical modulation is highly dependent on the probe frequency, with the strongest effects seen near the band edge of GaAs due to the band tailing effect.

In diamond crystals, we have seen a strong modulation of the reflectivity signal in the ion-bombarded specimens. The modulations suggest an increase in the real refractive index, which is unusual in ion-bombarded materials due to density considerations; a strong increase in the absorptivity of the specimens; and a sign reversal of the p_{12} component of the photoelastic tensor. These results will aid in the construction of diamond-based quantum information systems using ion implantation methods.

Spin-Coherent Transport under Strong Spin-Orbit Interaction

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Funding: $100,000

PROGRAM SCOPE

The project aims to gain fundamental insight in quantum-coherent spin-dependent phenomena arising from spin-orbit interaction, via experiments on nanolithographic solid-state samples. Spin-orbit interaction in the solid-state can provide an avenue for spin operations in quantum information processing and for the generation of new quantum states of matter. The experiments use electronic transport in structures at mesoscopic length scales approaching the mean free path and the quantum phase- and spin-coherence lengths. Materials employed comprise semiconductor and semimetal systems with strong spin-orbit interaction and long quantum coherence at low temperatures; two-dimensional electron systems in the semiconductors InAs, InGaAs, and InSb; and thin-film semimetal bismuth. Objectives include a study of the effect of reduced dimensions on spin coherence under spin-orbit interaction. Objectives also comprise the characterization of the Aharonov-Casher quantum-mechanical phase and its associated vector potential, particularly as generated by the confining electric fields at the boundaries of mesoscopic spin-coherent samples. The Aharonov-Casher phase is the electromagnetic dual of the Aharonov-Bohm phase, and is obtained by exchanging the magnetic fields and electric charges appearing in the Aharonov-Bohm phase by electric fields and magnetic moments (spin). The objectives also include a study of the semimetal bismuth and of its strongly spin-orbit coupled surface states. Bismuth is relatively unexplored as a material for phase-coherent and spin-coherent thin-film mesoscopic structures. Objectives hence aim at the fabrication and characterization of bismuth thin-film mesoscopic devices to explore the effect of the strong spin-orbit interaction in quantum coherent structures. The project utilizes electronic transport measurements over variable temperatures and under magnetic fields on samples prepared by nanoscale fabrication techniques. Presently the approach allows a deeper understanding of spin phenomena and quantum interactions in solids. As a long-term impact, the insights will be valuable in the development of future magnetoelectronic and spintronics device functionalities.

FY 2012 HIGHLIGHTS

An optimized method was developed to deposit bismuth films with bulk-like quality on insulating amorphous SiO2. Thin films form a starting point for the fabrication of bismuth quantum- and spin-based devices. The optimization was guided by measurements of electrical transport coefficients, of quantum phase and spin coherence, and of structural properties of the films. A two-stage growth procedure was found to optimize the film properties. An initial wetting layer, proceeded by island growth, is deposited at a lower temperature, followed by a high-quality active layer at a higher temperature. An approximately 100 nm film was found to optimize both bulk-like bismuth characteristics and the two-dimensional quantum coherence properties desired for bismuth quantum devices.

Time-Resolved Spectroscopy of Insulator-Metal Transitions: Exploring Low-Energy Dynamics in Strongly Correlated Systems

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Funding:	$150,000

PROGRAM SCOPE

The phase complexity in doped manganites makes the investigation of periodic layered structures especially intriguing, given the possibility of engineering charge, spin and orbital ordering in a layer-by-layer manner. Such structures may lead to new phases, spin canting, and spin frustration due to charge transfer, as well as strain effects and exchange interaction across atomically sharp interfaces. Moreover, such phases are potentially controllable through stress, optical excitation, electric and magnetic fields. A major thrust of this project is to determine the interface magnetic anisotropy and switching characteristics in various manganite thin-film heterostructures using the interface-specific magnetization-induced second-harmonic generation (MSHG) technique. We will apply a biasing electrical field in these structures to modify the amount of charge transfer at the interfaces and to correlate the tailored electronic structure to the interface magnetization obtained by MSHG measurements. We will also perform time-resolved measurements to study the ultrafast dynamics and coherent precession of the interface and bulk magnetization in these heterostructures, which are important issues in determining the performances of spintronic devices. A coherent manipulation of the magnetization enhances the operational speed of these device structures.

FY 2012 HIGHLIGHTS

A new mechanism has been discovered that holds promise for fast switching of the magnetization in novel magnetic recording and magneto-electronic devices. Using time-resolved magneto-optical Kerr effect measurements, we observed large magnetization precessions over a wide range of applied magnetic fields (0-2.5 T) in ferromagnetic $La_{0.67}Ca_{0.33}MnO_3$ (LCMO) thin films grown on $NdGaO_3$ substrates. Pronounced spin precessions are also excited at zero field and in the geometry with negligible canting of the magnetization, i.e., when the field is applied along the in-plane easy axis which provides significant advantages for device applications. The excitation of ultrafast magnetization precessions in the LCMO film can be reasonably explained by the emergence of antiferromagnetic interactions caused by charge transfer and alteration of kinetic energy of itinerant electrons in LCMO under optical excitation. We thus propose a transient exchange field that triggers the spin precession. This result provides new insight into the role of exchange coupling on the fast magnetization dynamics and switching in novel complex oxide materials. These properties make them ideal candidates for a broad range of new enabling technologies, e.g., magnetic storage, efficient energy transmission, novel electronic and magnetic devices, and quantum computing.

Atomic Layer Controlled Growth of Pnictide Superconducting Thin Films Heterostructures by Design

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Sr. Investigator(s):	
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Funding:	$100,000

PROGRAM SCOPE

The discovery of superconductivity with transition temperatures of 20K-50K in iron-based materials has initiated a flurry of activity to understand and apply these novel materials. The superconducting mechanism, structural transitions, magnetic behavior above and below T_c, doping dependence, and critical current and flux-pinning behavior have all been recognized as critical to progress toward understanding the pnictides.

A fundamental key to both basic understanding and applications is the growth and control of high-quality epitaxial thin films. The ability to control the orientation, the strain state, defect and pinning site incorporation, the surface and interfaces, and potentially the layering at the atomic scale are crucial in the study and manipulation of superconducting properties. Our main tasks are to control pnictide thin film and oxide templates at the atomic level, to understand the relation between structure and superconducting properties, and to design and grow novel crystalline pnictide heterostructures 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 thin film and superlattice synthesis of pnictide films on oxide templates by pulsed laser deposition with in situ high pressure RHEED, to investigate fundamental superconducting properties of pnictides; (2) strain engineering for control and investigation of superconducting properties, (3) understanding and control of flux-pinning mechanisms, and (4) pnictide grain boundary engineering.

FY 2012 HIGHLIGHTS

We have grown artificially layered superlattice structures in Co-doped Ba-122 thin films with controlled structural and compositional modulations. The insertion of O-Ba-122 layers allows nanoparticle formation that introduces strong vortex pinning along the *ab*-planes while still allowing the formation of vertically-aligned defects. The remarkable enhancement of the pinning properties over a wide angular range related to the *ab*-plane nanoparticles is highlighted by the significant increase of the irreversibility field and by much improved J_c. The engineered structures presented here are surely capable of further refinement by optimizing interlayer separation and the composition of the vortex pinning layers features which cannot be obtained in single layer films. The successful growth of such high quality artificially layered structure will have wide implications for achieving new interface-driven high T_c superconductivity and potential device applications involving SNS and SIS junctions. Furthermore, artificially made multilayer structures can also be used as model systems to study many physical phenomena such as dimensionality, proximity effect, and interface pinning.

DOE National Laboratories

Complex States, Emergent Phenomena, and Superconductivity in Intermetallic and Metal-Like Compounds

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Students:	4 Postdoctoral Fellow(s), 8 Graduate(s), 7 Undergraduate(s)
Funding:	$2,438,500

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 2012 HIGHLIGHTS

The Complex States, Emergent Phenomena & Superconductivity in Intermetallic and Metal-like Compounds (Complex States) FWP helped define and answer key physical questions about Fe- and Cu-based high temperature superconductors as well as strongly correlated, magnetic systems. Its members were responsible for ~60 peer reviewed publications, and its contributions to the field were acknowledged in the forms of Paul Canfield being presented the DOE Lawrence Award, John Clem being presented the IEEE Council on Superconductivity's 2012 Materials Award, and Rulan Prozorov becoming a Fellow of the American Physical Society.

The Complex States FWP was able to develop several key model systems for understanding the mechanisms associated with Fe-based superconductivity. Detailed studies of cobalt substituted $CaFe_2As_2$ (a compound discovered by this FWP) have demonstrated these materials' extreme pressure, processing, and compositional sensitivity and allow for strain tuning of the superconducting state at ambient pressure. Potassium substitution of $BaMn_2As_2$ has allowed for the creation of the first metallic, MnAs based analogue to the FeAs compounds and is allowing for more direct comparison to CuO-based superconductivity. Precise measurements of the high frequency properties of phosphorous substituted $BaFe_2As_2$ have underscored the importance of magnetic fluctuations, and the suppression of long-range magnetic order to the superconducting state and angle resolved photoemission spectroscopy (ARPES) measurements on ruthenium substituted $BaFe_2As_2$ have revealed the possibility of a new mechanism for suppressing these fluctuations and inducing superconductivity. More precise control and understanding of the superconducting state was also achieved through advances in the theoretical modeling of the anisotropic, upper superconducting critical field and through calculations that revealed how to improve the performance of superconductors in microelectronic applications. Technically, the Complex States FWP was able to complete the construction of a tunable vacuum, ultraviolet, laser system for an in-house ARPES spectrometer based on U.S.-grown KBBF nonlinear crystals. This is one of only two such tunable VUV laser systems in the world and the only one in the U.S. It will allow for greatly enhanced resolution, penetration depth, and throughput. In addition, the FWP commissioned a set of inert atmosphere glove boxes for the growth and characterization of reactive element based compounds.

Photonic Systems

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Funding:	$693,000

PROGRAM SCOPE

Since ~1990, the Ames Laboratory pioneered the development 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 commence exploration of organic spintronics. There will be a close synergy between theory, simulation, fabrication, and experimental studies in these interrelated tasks.

FY 2012 HIGHLIGHTS

We demonstrated extremely efficient indium tin oxide (ITO)-free OLEDs fabricated on a multilayer organic conductor resulting from a “strong weak microcavity” effect. [M. Cai et al., “Extremely efficient indium-tin-oxide-free green phosphorescent organic light-emitting diodes,” *Adv. Mater*. 24, 4337 (2012)]

We fabricated and characterized metal-coated woodpile PCs at NIR to optical region, with 600 nm period and < 100 nm resolution. Using sol-gel chemistry, direct laser writing, and electroless plating metallization techniques, we created the polymer network, fabricated the structures, and metalized them selectively. The structures showed ohmic behavior and a photonic gap in the visible region of the spectrum. This is the first time that 3D metallic structures with bandgap in the visible range were fabricated, opening the way for the design and fabrication of 3D optical components, isotropic optical metamaterials, and optical sensors. [N. Vasilantonakis et al., "3D Metallic Photonic Crystals with Optical Bandgaps," *Adv. Mater*. 24, 1101 (2012)].

A computational scheme was developed for a self-consistent treatment of 2D PCs, 3D PCs, and plasmonics systems with gain incorporated into the nanostructures. This method can help understand if introducing gain materials in metamaterials can reduce the losses and obtain lasing in PCs and plasmonics. [A. Fang et al., "Overcoming losses of a split ring resonator array with gain," *Opt. Express* 19, 12688 (2011); A. Fang et al., "Loss compensated negative index materials at optical wavelengths," *Photonics and Nanostructures* 10, 276 (2012)]

Surface Structures Far From Equilibrium

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Funding:	$578,000

PROGRAM SCOPE

The emergence of novel properties in nanostructures can be related to various factors, important ones being electron confinement and lower atom coordination. These properties can be substantially different from bulk properties. The goals of this FWP are two-fold, first to grow epitaxially controllable nanostructures and second to use their tunable properties on several technologically important problems. Understanding metal growth on graphene and other carbon coated substrates is one of the areas pursued. Graphene-based devices require stable metal contacts of low electrical resistance, and it is essential to identify growth conditions for uniform metal morphology. Controlling nanostructure thermal stability of metals on graphene is relevant for catalytic applications. 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. Finally, the expected enhanced reactivity of adsorbed gases on metal nanoislands is also investigated (i.e., hydrogen adsorption on Mg islands relevant to hydrogen storage and oxygen, ethylene adsorption on Ag islands relevant to ethylene epoxidation).

FY 2012 HIGHLIGHTS

With STM experiments and DFT calculations, metal growth (Gd, Dy, Eu, Fe, Pb) was used to extract the metal graphene interaction. For practically all metals, the grown islands are 3-d as a result of the low ratio of the metal adsorption energy on graphene to the metal cohesive energy. The growth of Fe was found to be unusual because it does not follow classical nucleation. The nucleated island density is unexpectedly high, it increases continuously with deposited amount θ, and is temperature-independent.

The island density becomes tunable with θ, which can be useful in magnetic storage applications. *PRL.* 109, 026103 (2012).

Thermal annealing of the metal islands on graphene shows limited coarsening with the island density almost unchanged, but with increasing aspect ratio (height/lateral size) which can be useful for catalytic applications *PRB* RC 86 081414 (2012).

Patterns of Ag nanostructures were created on Si-(111)-Ag(√3x√3) by first creating defects with STM pulses, followed by Ag deposition at room temperature. Because of the large diffusion length of Ag, it selectively aggregates at defects at the pre-selected locations. The size of the smallest Ag features is ~2 nm. J*. Vac. Sci. Technol. B* 30 050601 (2012).

Using STM, the effect of oxygen exposure on an ensemble of Ag islands grown on Si(111)-(7x7) was studied. The preferred height for the clean Ag islands is 2-layers. By exposing the surface to oxygen, 3-layer islands are favored, which shows that it is possible to manipulate the preferred height. The Ag islands are clean, free of oxygen, and only the wetting layer shows evidence for oxygen adsorption. *Surf. Sci*. (606)1871(2012).

Digital Synthesis - A Pathway to Create and Control Novel States of Condensed Matter

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Funding:	$720,000

PROGRAM SCOPE

Interfaces between complex oxides provide a unique environment where the charge, spin, and lattice degrees of freedom may “reconstruct,” giving rise to novel states of condensed matter. In our research program, we seek to create, explore, understand, and manipulate these states. We use digital synthesis, where we create superlattices and heterostructures by interleaving integer layers of the constituent materials, and all charge transfer or doping takes place at atomically sharp interfaces. We will explore properties of materials that are known to have interesting collective phases, such as the manganites, nickelates, and titanates, where the effects of disorder have been engineered away by digital synthesis. We shall explore two-dimensional Ruddlesden-Popper phases where dimensional confinement gives rise to novel behavior. We seek to create and discover materials that are on the verge of a transition and tune these with external fields and currents. Lastly, we will explore a new class of materials in the 5d transition metal oxides, where strong spin-orbit interactions play a definitive role. This leads to novel correlated insulators and may give rise to superconductors and topologically protected surface states according to theoretical predictions. We will synthesize materials using state-of-the-art, ozone-assisted oxide Molecular Beam Epitaxy at Argonne and characterize them using a comprehensive set of tools, including magnetic and transport measurements, x-ray, and neutron scattering and electron microscopy. This project is jointly funded by BES Synthesis and Processing Science and Experimental Condensed Matter Physics.

FY 2012 HIGHLIGHTS

We realized a delta-doped ferromagnet in an antiferromagnetic (AF) manganite by adding a single atomic layer of electron dopants to the antiferromagnet. The ferromagnet was shown to form via canting of the AF spins. This was the first direct demonstration of an idea proposed by de Gennes. We exploited this to create a quasi-2D region of ferromagnetism, in a manner that is unique to the mechanism of double exchange ferromagnetism. We also wrote a detailed review of the physics of manganite heterostructures.

Emerging Materials

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Funding:	$1,345,000

PROGRAM SCOPE

Emerging Materials couples materials synthesis to insight-driven science as its strategy for fundamental condensed matter research. Within this synthesis-science dyad, our program is extending beyond its work on 3d transition metal oxides (TMO)—in which spin, charge, and orbital sectors are distinct, identifiable, and measurable—to address 5d systems that lie beyond the regime of ‘delicately balanced and tightly coupled’ interactions found among these sectors. We use high quality single crystals grown within our program to explore how relativistic spin orbit coupling entangles these notionally separable spin-, charge-, and orbital-order parameters so as to expose new quantum phases in the presence of electron correlation in 5d oxides. Specifically, we are exploring metal insulator transitions in the presence of this entanglement and searching for links to unconventional superconductivity. We are building frustrated lattice structures in both 3d and 5d compounds to expose spin-sector and spin-lattice sector interactions for insights into control of magnetic short-range order. We use reduced dimensionality to test the generality of magnetic and electronic phase segregation, and are exploring non-equilibrium transport effects in both 3d and 5d systems, as part of an overarching objective of bridging the gap between the separable and mixed facets of competing interactions.

FY 2012 HIGHLIGHTS

In heavy transition elements, spin and orbit merge into a composite ‘spin-orbit coupled’ state. We have shown using RIXS at the APS that in Sr_2IrO_4 and $Sr_3Ir_2O_7$ these composite moments behave as if they have north and south poles, completely analogous to that of classical bar magnets. This `dipolar’ effect is enhanced by tuning the crystal structure until it lies on the border between a metal and an insulator. The result is an unprecedented energy gap in the magnetic excitation spectrum, demonstrating that the conventional view of charge interactions dominating over spin interactions need not apply when spin-orbit coupling is strong.

In the case of Sr_2IrO_4, RIXS also revealed excitations that were attributed to (1) spin-waves at low energy and (2) ‘flipping’ of the spin relative to the orbital moment at high energy. We also showed the low-energy magnetic excitation propagates through the crystal lattice with a form very similar to the spin waves characteristic of high T_c superconducting cuprates. The high-energy excitation propagates like a doped hole in a background of antiferromagnetically ordered spins—a scenario also played out in the high T_c materials. The similarity borne by both excitations to features characteristic of the cuprates reinforces speculation that appropriate doping of electronic carriers into Sr_2IrO_4 could lead to a new class of unconventional superconductors.

Magnetic Thin Films

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Funding:	$1,990,000

PROGRAM SCOPE

The issues our group addresses in nanomagnetism encompass (1) spin dynamics, (2) spin transport, and (3) the creation of new multilayer materials, based on metallic heterostructures. Our program in spin dynamics provides insights into artificial magnonic materials. The work advances our fundamental understanding of linear and nonlinear excitations in magnetic nanostructures. Our program in spin transport focuses on the physics of pure spin currents. Recently, spin currents have been recognized as a way to communicate without charge currents, potentially eliminating wasted heat that impedes further transistor miniaturization. Due to this heat, information technology is an energy technology issue as well as a U.S. economic competitiveness issue.

Finally, the quest for new functional materials via nanoscale multilayering enables us to create systems that possess unusual synergistic properties that may otherwise be mutually exclusive. Such systems include exchange spring composites with low or no rare-earth content than can exceed today’s commercial capabilities as used in electric motors and generators, or ferromagnetic-superconducting multilayers that support an exotic interfacial pairing even though the individual components can be as simple as elemental layers. Such multilayering also enables us to explore the energetics and transport mechanisms underlying organic spintronic heterostructures. These concepts and the materials explored within this proposal also provide samples worthy of advanced characterization at BES major characterization facilities.

FY 2012 HIGHLIGHTS

Utilizing a 2D array of non-interacting Permalloy (Py) dots, we showed, theoretically and experimentally, that patterning can dramatically enhance the nonlinear properties, which provides a pathway to a new class of artificial magnetic metamaterials. We investigated, via experiment and micromagnetic simulations, dynamic interactions between coupled vortices in connected double-dot structures. We found that vortex resonance frequencies can be tuned by varying the overlap area between dots. We refined our spin Hall effect measurements to generate spin currents via spin pumping, enabling our investigation of ferromagnetic proximity effects in polarizable Pt or Pd structures. While spin waves generally only travel in a straight trajectory, we created conduits with an integrated electrical conductor to provide local magnetic fields that transport the spin waves through curved waveguides. The anomalous Nernst effect generates a *dc* voltage perpendicular to the magnetization and temperature gradients in ferromagnetic wires. We showed that this magneto-thermoelectric signal enables the high signal-to-noise detection of spin waves. For ferromagnetic-superconducting hetero-structures, we observed an enhancement of T_c as the Py domain wall is twisted via rotating a magnetic field.

Superconductivity and Magnetism

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Students:	0 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$2,084,000

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 so as to promote use-inspired innovations.

We investigate materials from macroscopic to 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 iron pnictides, which embody a new opportunity in the search for an isotropic high temperature superconductor. Another grand challenge is to develop novel strategies for controlling vortex dynamics by creating active, adaptive, and smart vortex pinscapes to tailor the electromagnetic behavior of type II superconductors. In addition, we are seeding new research into the spectral character of THz radiation from high temperature superconductors, which has the potential for a new compact and portable THz source. We maintain leading programs in experiment and theory, with each deriving strong benefit from close mutual cooperation. Our present research focuses on (1) exploring the multi-band nature of iron-based superconductors, (2) developing nano-pinscapes to control vortex pinning and liquid flow, (3) investigating complex phenomena at the interface of superconductivity and magnetism in hybrid heterostructures, and (4) elucidating the physics of coherent THz electromagnetic wave generation by intrinsic Josephson junctions in crystal micro-mesas.

FY 2012 HIGHLIGHTS

We made progress in all the four research areas listed above. (1) We conducted the first systematic specific heat measurements on a series of $BaFe_2(As_{1-x}P_x)_2$ single crystals with phosphorous doping ranging from x = 0.3 to 0.55. Our results reveal that $BaFe_2(As_{1-x}P_x)_2$ follows the scaling $\Delta C/T_c \sim T_c^2$. The clean-limit nature of this material imposes new constraints on theories aimed at explaining the scaling. (2) We discovered a new dissipation mechanism due to current-excited moving vortices in superconducting niobium strips with a chain of nanoscale holes. In addition, we carried out magneto-transport measurements and computer simulations to elucidate the saturation number and caging effect in a superconducting film containing a honeycomb array of nanoscale holes. (3) We demonstrated the slowing down of vortex dynamics due to both Foucault currents and remagnetization processes induced by moving vortices in a novel Nb/Py hybrid structure. (4) We demonstrated that free-space radiation powers of ~0.6 mW at THz-frequencies can be generated from intrinsic Josephson junctions in BSCCO when several resonator shaped samples are synchronized. Theoretical modeling suggests that the synchronization between the resonators occurs through electromagnetic waves traveling in the substrate underneath the resonators.

Atomistic Transport Mechanisms in Aluminum-Based Hydrides

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Funding:	$700,000

PROGRAM SCOPE

This research program is focused on understanding hydrogen-aluminum interactions, atomic transport, and the effects of catalysts in the formation of Al-based hydrides. The first thrust of the proposed research is to understand the atomic-scale effects of hydrogen with catalyzed light metals (e.g., Al) and to explore how complex reaction environments affect and control these fundamental interactions. The second thrust will build upon and utilize our understanding of Al-H interactions on Ti-doped Al surfaces to investigate alane formation in the presence of a stabilizing ligand (e.g., amine) and develop new procedures for the formation of solid AlH_3 and other metastable aluminum-based hydrides (e.g., $Mg(AlH_4)_2$).

We use complementary high-resolution microscopy and spectroscopy in close connection with theory to probe hydrogen metal interactions and hydrogenation near technologically relevant conditions. We are addressing the following scientific areas: (1) atomic processes associated with hydrogen uptake and release kinetics, (2) the role of surface structures and chemistry in affecting hydrogen-materials interactions, (3) the effect of dopants, (4) the formation of alanes, and (5) the structure and bonding of alane and alanate amine adducts. The development of experimental techniques for isolating atomic- and molecular-level processes in complex environments, such as high-pressure H_2 gas or liquid H_2-containing solutions, will significantly expand our ability to investigate the interaction of hydrogen with materials.

FY 2012 HIGHLIGHTS

The formation of LiAlH4–THF by direct hydrogenation of Al and LiH in tetrahydrofuran (THF) was investigated using spectroscopic and computational methods. The effectiveness of two types of catalysts, titanium chloride ($TiCl_3$) and titanium butoxide ($Ti(C_4H_9O)_4$), and the catalyst concentration were evaluated under similar reaction conditions. These results have indicated that although a small amount of Ti is necessary for disassociating H_2, excess surface Ti (>0.1 ML) hinders the formation of Al–H species (published in PCCP, 2012).

$(NMPy)_2\cdot AlH_3$, $NMPy\cdot AlH_3$, and $NEPy\cdot AlH_3$ (NMPy = *N*-methylpyrrolidine, NEPy = *N*-ethylpyrrolidine) were synthesized from titanium doped aluminum metal and H_2 gas in $NMPy/Et_2O$ and $NEPy/Et_2O$ solution.

NMR and infrared spectroscopy and x-ray powder diffraction were used to characterize the complexes and monitor the decomposition processes. The reversible formation of $(NMPy)_2 \cdot AlH_3$ from Al* and NMPy under 1000 psi hydrogen was observed while no alane formation was detected with NEPy. Theoretical calculations indicate that these dramatic differences are caused by steric effects imposed by the ethyl group in NEPy. The thermal decomposition of these complexes in the presence of one equivalent of LiH readily gives $LiAlH_4$ in nearly quantitative yields at 50°C under reduced pressure.

Complexity from Simplicity: Quantum Criticality and Novel Collective Phases in Itinerant Ferromagnets

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Funding:	$550,000

PROGRAM SCOPE

The need to understand the collective instabilities resulting from electronic interactions and to harness the resulting emergent behaviors, such as superconductivity and magnetism, are the central motivations for this research. The most extreme electronic correlations are found near quantum critical points, where the suppression of competing phases and incipient electronic localization that are driven by strong interactions lead to new collective phases, such as unconventional superconductivity. We will investigate the extent to which this scenario, developed for strongly correlated materials like cuprates, heavy fermions, and iron pnictides, is universal, i.e., appropriate for more conventional materials with weaker correlations. Developing a holistic phase diagram that is suitable for materials with different correlation strengths, where superconductivity and magnetism are separate regimes, will provide direction for the discovery of new materials with purpose-built functionality, which are the feedstock for advancing new technologies for sensor and device applications, as well as energy conversion and distribution applications.

FY 2012 HIGHLIGHTS

We have discovered a new system YFe_2Al_{10} where proximity to a ferromagnetic quantum critical point is evidenced by unusual divergencies in magnetic susceptibility and specific heat, matched by field-temperature scaling that established that both are critical variables. NMR and inelastic neutron scattering measurements show that the critical modes are ferromagnetic. These data are a challenge for current theory, which find that ferromagnetic order disappears at a first order transition where critical fluctuations are weak. We have also synthesized single crystals of the half-metallic system Fe_2TiSn, the first ever single crystal of the 3d-electron Heuslers, and investigations of its criticality are underway. Finally, we have shown that electron doping can drive the correlated insulator $FeGa_3$ through a first order metal-insulator transition that can be reversed by magnetic fields.

Electron Spectroscopy

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Students:	1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$1,800,000

PROGRAM SCOPE

The Electron Spectroscopy Group's primary focus is on the electronic structure and dynamics of condensed matter systems. The group carries out studies on a range of materials, including strongly correlated systems and thin metallic films. A special emphasis is placed on studies of High Tc superconductors, topological insulators (TIs), and low dimensional systems such as graphene. The primary techniques used include high-resolution photoemission and infra-red spectroscopy or optical conductivity. The experiments are carried out both within the laboratories in the Condensed Matter Physics and Materials Science Department and at the National Synchrotron Light Source using both synchrotron radiation and laser based sources. The emphasis is on the study of the low energy excitations and the nature of the interactions of the latter with their environment.

FY 2012 HIGHLIGHTS

Three-dimensional TIs have Dirac-like surface states in which the spin of the electron is locked perpendicular to its momentum in a chiral spin-structure where electrons with opposite momenta have opposite spins. A direct consequence is that backscattering, which would require a spin-flip process, is not allowed if a time- reversal- invariant perturbation, such as non-magnetic disorder, is present. This makes the surface states promising candidates for spintronics and quantum computing applications, where spin-coherence is crucial. While elastic scattering imposes the ultimate limit on charge transport, the inelastic scattering processes dictate a material's transport properties at finite temperatures. In particular, interactions of electrons with the lattice modes are responsible for increasing resistivity with temperature in conventional metals, and there is no reason why this should not happen in TIs. Angle-resolved photoemission spectroscopy, an experimental technique that measures momentum resolved scattering rates directly, has been used to show, contrary to these expectations, that the electrons on the surfaces of these new materials are also "protected" from scattering on lattice vibrations and remain coherent, even at ambient temperatures. This suggests that topological insulators could serve as the basis for wide-spread applications in room temperature electronic devices.

An optical study of the superconductor KFe_2Se_2 revealed that this material was semiconducting in character, with a weak metallic component. This material is in fact inhomogeneous, with a small metallic fraction (~10%) in an insulating matrix. Clean limit systems violate the universal scaling relation. By considering an inhomogeneous granular superconductor, an optical conductivity study found that a superconductor in the clean limit will mimic one in the dirty limit, and will in fact obey the universal scaling relation.

Spectroscopic Imaging STM & Complex Electronic Matter Studies

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Funding:	$320,000

PROGRAM SCOPE

This program focuses on (1) topological superconductivity and, more importantly, topological surface states in Sr_2RuO_4—the only known topological superconductor; (2) the search for new topological superconductors in CuBi2Se3 and Bi0.32Sb0.16Pb0.32Te0.2; (3) visualizing quantum critical electronic matter in heavy fermion compounds such as $YbRh_2Si_2$, (4) high precision transport/thermodynamic measurements of novel and complex forms of electronic matter, for example, spin liquids and monopole fluids.

FY 2012 HIGHLIGHTS

Efforts made during Fiscal Year 2012 include (1) spectroscopic imaging STM studies of energy gap structure in topological superconductor in Sr_2RuO_4; (2) spectroscopic imaging STM studies of energy gap structure in, what turned out to be, non-topological superconductor $CuBi_2Se_3$; (3) measured density of electronic states within the quantum critical electronic matter in heavy fermion compound $YbRh_2Si_2$; and (4) development of new cryostat and instruments for high precision transport/thermodynamic measurements of spin liquids and monopole fluids.

A Synergistic Approach to the Development of New Hydrogen Storage Materials. Part II: Nanostructured Materials

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Funding:	$268,000

PROGRAM SCOPE

The Berkeley Hydrogen Storage Program consists of a broad-based, multi-investigator effort for developing new types of hydrogen storage materials. Our approach is to explore numerous possibilities for new materials, and the synergy of many scientists in one location working toward a common goal is expected to accelerate progress and lead to new ideas via cross-fertilization. The present proposal represents a renewal of the funding for half of the program, which focuses on the development of new nanostructured materials of potential utility in hydrogen storage applications. Specific areas for investigation include: synthesis of new nanostructured boron nitride and graphene-based materials, fundamental measurements of H_2 uptake in single nanocrystals, synthesis and evaluation of H_2 uptake in magnesium-based nanocrystals, and development of nanocrystal/metal-organic framework hybrid materials for probing hydrogen uptake via a spillover mechanism. Our existing hydrogen storage characterization facility will be maintained in order to provide accurate and immediate feedback on the many new materials generated. Ultimately, this research is expected to yield materials that could possibly enhance the range of hydrogen fuel cell-powered vehicles.

Magnetic Materials Program

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Students:	3 Postdoctoral Fellow(s), 3 Graduate(s), 0 Undergraduate(s)
Funding:	$2,405,000

PROGRAM SCOPE

Our objectives are the development of a basic understanding of novel nano- and meso-scale magnetic structures and strongly correlated magnetic materials, and the exploration of new phenomena permitting the control of spins down to fundamental magnetic length and time scales. This research will not only provide answers to grand challenge questions, such as how new magnetic properties of matter emerge from complex correlations at the nanoscale and how those can be engineered and controlled, but how the understanding of nanoscale behavior can be used to discover new magnetic properties and phenomena at multiple length, time, and energy scales extending into meso-scales. Whereas this research is primarily knowledge-inspired, new spin-based materials, structures, and phenomena will serve the development of spintronics devices with significantly enhanced functionalities, energy efficiency, and processing speed.

We will achieve these goals using a unique combination of state-of-the-art synthesis and a powerful range of characterization techniques (x-ray spectromicroscopy, photoemission, scattering, and nanocalorimetry) providing spatiotemporal imaging, elemental selectivity, depth sensitivity, and thermodynamic measurements, supported by multiple theoretical efforts.

In prototypical systems, we will study the impact of surfaces and interfaces on magnetic behavior, the microscopic origins of magnetic phase transitions, the relation between heat and spin currents, and the spin dynamics of coupled magnetic nanostructures.

By expanding our research into ultrafast time scales and studies of magnetic systems far from equilibrium, we will lay groundwork for new opportunities at future large scale facilities.

FY 2012 HIGHLIGHTS

We have shown, by x-ray microscopy and photoelectron spectroscopy, that the AFM to FM transition in FeRh exhibits on a microscopic scale a coexistence of both phases and is further accompanied by significant changes in the electronic structure over the entire valence-band region. We have investigated the bulk electronic structure in the prototypical dilute magnetic semiconductor $Ga_{0.97}Mn_{0.03}As$, with our hard x-ray angle-resolved photoemission data solving a controversy in showing that ferromagnetism must take into account both p-d exchange and double exchange. We have identified a symmetry breaking effect in the nucleation of magnetic vortex structures in arrays of magnetic permalloy thin film disks by high resolution soft x-ray microscopy data, which can be linked to an intrinsic Dzyaloshinskii-Moriya interaction breaking the inversion symmetry near the disk surface.

In the future, we will explore whether strain can be used to tailor the AFM-FM transition in an BFO-FeRh multilayer systems, thus aiming for electrically-tunable magnetic transitions; we will investigate the physics behind a radically improved field-switchable magnetic tunnel junction with perpendicular anisotropy with our x-ray standing wave photoemission approach; and we will study whether we can trigger a symmetry breaking effect in shaped-biased magnetic disks.

Novel sp2-Bonded Materials and Related Nanostructures Program

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Students:	1 Postdoctoral Fellow(s), 4 Graduate(s), 0 Undergraduate(s)
Funding:	$1,085,000

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 sp2-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 sp2-based and other nanoscale materials. This program also seeks to develop specialized instrumentation for synthesis, characterization, and applications.

FY 2012 HIGHLIGHTS

Thus far, the sp2 program has successfully developed a new kind of environmental TEM imaging cell, the Graphene Liquid Cell (GLC), which allows atomic-scale imaging of molecules and nanostructures in liquid environments. The in-situ growth of Pt nanocrystals has been thus characterized. In the next period, it is anticipated that this technology will be expanded to include statics and dynamics of other nanosystems, including alloys and biomaterials.

Quantum Materials Program

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Students:	7 Postdoctoral Fellow(s), 4 Graduate(s), 0 Undergraduate(s)
Funding:	$1,433,000

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 interacting 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 (1) extensive thin film and bulk crystal fabrication capabilities; (2) advanced characterization tools, including ARPES, ultrafast optical pump/probe, neutron and x-ray scattering, and transport and thermodynamic measurements; and (3) a theory group whose members are leaders in predictive and phenomenological methods.

FY 2012 HIGHLIGHTS

We are making substantial progress in our effect to understand quasiparticle and collective dynamics in cuprate superconductors. In collaboration with the Greven group at U. Minnesota, we are studying the model *e*-doped cuprate, $Nd_{(2-x)}Ce_xCuO_{(4+\delta)}$, where we are observing critical slowing down with approach to a quantum critical point. In addition, we are performing simultaneous time-resolved ARPES and optical measurements of recombination and gap dynamics on a variety of cuprates. Preliminary results are revealing strong momentum dependence of quasiparticle lifetimes. In the area of Fe-based superconductors, we are performing neutron scattering studies of the $BaFe_2As_2$ system with isoelectronic doping, substituting Ru for Fe. The initial results suggest that the superconductivity in this system is achieved by progressively decreasing the strength of electron-electron interactions.

We have achieved a long-term goal of developing a revolutionary instrument for spin-resolved photoemission based on low-energy exchange scattering and time-of-flight energy analysis. This instrument, the first of its kind, provides nearly hundred-fold increase in sensitivity over commercially available instruments. The sensitivity is sufficiently high that combined time- and spin-resolved measurements are now feasible, constituting a unique system for probing spin dynamics. Work has begun this year on a new focus for the group, strongly spin-orbit coupled crystals and thin films. In iridate thin films, we have observed systematic variation in conductivity with strain applied by epitaxial growth on different substrates. In the chiral Dzyaloshinskii-Moriya metals, MnSi and FeCoSi, we have observed helimagnon modes by time-resolved Kerr effect measurements.

Electron Correlation in Complex Systems

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Funding:	$600,000

PROGRAM HIGHLIGHTS

This OBES program was active between 1995 and 2012. Work resulted in 121 publications; 80 peer reviewed publications, including 8 Phys. Rev. Letters and 12 Pys. Rev. Bs; 38 conference proceedings; 3 editorships; and 70 invited talks at conferences and workshops, including 32 international. The most important findings are presented in the following publications:

(1) “Evidence of Dynamical Spin Shielding in Ce from Spin-resolved Photoelectron Spectroscopy,” *EuroPhysics Letters* 77, 17004 (2007).

(2) “Orbital Specificity in the Unoccupied States of UO2 from Resonant Inverse Photoelectron Spectroscopy,” *Phys. Rev. Lett*, 107, 167406 (2011).

Quantum Electronic Phenomena and Structures

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Funding:	$140,000

PROGRAM SCOPE

The overall goal of this project, undertaken in collaboration with researchers at Sandia National Laboratories, is to explore novel quantum phenomena in unique low-dimensional semiconductor structures. Within this project, our focus is to study quantum nanophotonic and nanoelectronic structures using ultrafast optical techniques. To this end, we have examined ultrafast carrier dynamics in several nanowire (NW) systems, including Ge, Si, and GaN. Our recent efforts have centered on optical pump-probe experiments on III-nitride NWs, which are of great interest due to their potential applications in solid-state lighting and nanophotonics. In these experiments, we photoexcited GaN NWs above their band gap with a femtosecond ultraviolet pulse and tracked carrier relaxation into and out of the defect states responsible for the undesirable phenomenon of yellow luminescence (YL) with a visible probe pulse. This allowed us to show that carrier relaxation through the YL states increased with the NW growth temperature, likely due to the presence of additional impurity sites in NWs grown at lower temperatures [P. C. Upadhya, et al, *Semicond. Sci. Tech.* (2010)]. We also performed the first ultrafast optical experiments on individual nitride NWs, revealing a variation in carrier dynamics along the NW axis [P. C. Upadhya, et al, in *17th International Conference on Ultrafast Phenomena* (2011)].

FY 2012 HIGHLIGHTS

More recently, we have found that radial (core/shell) heterostructuring is a more desirable method of controlling carrier dynamics in GaN NWs. This was revealed when we performed UV-pump, visible-probe measurements on GaN, GaN/AlGaN, and GaN/AlN NW ensembles to examine carrier relaxation through the YL states. We found that photoexcited carriers in the GaN core-only NWs relax much more rapidly than in the GaN core/shell NWs, indicating that the shell passivates the surface defect states that trap carriers in the core-only NWs. In addition, we found that thinner AlGaN shells provided the best surface passivation, likely due to better lattice matching between the core and shell materials.

In parallel, we have improved our ultrafast optical microscopic experiments on individual Si NWs [M. A. Seo, et al, *Appl. Phys. Lett.* (2012)] by focusing our pulses through a microscope objective to obtain ~2 micron spatial resolution with concurrent sub-picosecond temporal resolution. This has enabled us to photoexcite an individual NW at a given axial position and probe at a different position, enabling us to track electrons and holes as they diffuse along the NW after the initial photoexcitation. From this, we were able to separately measure important parameters, such as the average diffusion coefficient, surface recombination velocity, and electron and hole diffusion currents, and also reveal acoustic phonon oscillations in single NWs for the first time [M. A. Seo et al, *Nano Lett*. (2012)].

Science of 100 Tesla

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Singleton, John, Los Alamos National Laboratory

Students: 2 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding: $835,000

PROGRAM SCOPE

This program employs the 100 T Multi-Shot Magnet (100TMSM) for investigating outstanding questions and emergent themes in condensed matter physics and materials science, and to search for new phenomena. Non-destructive magnetic fields of 100 T represent a considerable advance over pre-existing technologies, in that the sample and magnet survive thousands of pulses, and each pulse lasts thousands of times longer than in destructive 100 T magnets. These advances enable us to repeat a measurement at 100 T, providing for unprecedented reproducibility and precision because the sample is not disturbed or lost. The three-order-of-magnitude increase in pulse duration vastly reduces eddy-current heating in metals and magneto-caloric effects in magnetic systems, enabling studies at low temperature. Finally, the increased time at field is long enough to enable techniques such as specific heat, thermal conductivity, magnetostriction, and high-frequency conductivity.

The 100 T magnet provides a non-invasive, reversible probe that couples directly to the spin and orbital degrees of freedom of electrons in solids, producing significant energy shifts that disturb the basic energy balance of the system, inducing phase transitions and other effects. The energy shifts in 100 T fields match the scale of many of the robust electronic phenomena characterized by transitions occurring at temperatures ~100 K. High magnetic fields also provide a tunable magnetic length scale (l = (25.7/B1/2) nm) that parameterizes the spatial extent of the wavefunctions of band electrons. At 100 T, l is comparable to the smallest nanostructures or even moderately-sized organic molecules or to the vortex core size in high Tc superconductors.

FY 2012 HIGHLIGHTS

Fiscal year 2012 was a successful year for the 100 T program in that non-destructive magnetic fields exceeding 100 T (by a small margin) were achieved for the very first time and this was done in conjunction with several different condensed matter experiments. For example, in the non-magnetic perovskite LaCoO3, the transition into a magnetic high spin state regime was investigated, revealing multiple transitions above 60 T in the magnetization and strain. Multiple transitions reveal, for the first time, collective phenomena involving multiple spin states with different orbital arrangements. In the frustrated spin-dimer compound SrCu2(BO3)2, we obtained unambiguous evidence in the magnetization and strain for a transition into a state with one half of the fully saturated magnetization above 85 T. The simplicity of the magnetic superlattice associated with the highest magnetic field magnetization plateaux enables the relationship between order and geometric frustration to be understood. In the underdoped high temperature superconductor YBa2Cu3O6+x, we have observed magnetic quantum oscillations over an unprecedented range of magnetic fields (extending beyond 100 T) and over a broad range of angles in tilted magnetic field experiments, enabling the origin of the Fermi surface reconstruction to be resolved.

Towards a Universal Description of Vortex Matter in Superconductors

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Funding:	$645,000

PROGRAM SCOPE

Superconducting vortex physics became a major field in condensed matter physics since the discovery of the oxide high temperature superconductors (HTS). Vortex matter in HTS has a complex phase diagram in the magnetic field-temperature (H-T) space with a proliferation of solid and liquid phases and fast non-equilibrium dynamics. The rich vortex physics in HTS arises from the much larger influence of thermal fluctuations as compared to conventional low temperature superconductors (LTS), but it is important to notice that there is no hard boundary between LTS and HTS vortex phenomenology. The Fe-based superconductors provide the opportunity to "bridge the gap" between LTS and HTS by studying a large family of materials with broad ranges of parameters and properties. 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. Valuable information can also be obtained from MgB_2, a chemically simpler two-band superconductor. The central idea of this project is obtain a universal vortex physics description, applicable to all superconductors. Our focus is on interactions between vortices with material inhomogeneities, with emphasis on the influence of thermal fluctuations. Our project is fundamental-science oriented in terms of the methodology and expected outcome, but we intend to obtain results applicable to materials of technological relevance, including predictions valid for new superconductors that can be discovered in the future.

FY 2012 HIGHLIGHTS

We focused on the study of the effects of proton irradiation on the vortex properties of the “122” family of the iron-arsenide superconductors. We published three studies on this topic, on $Ca_{0.5}Na_{0.5}Fe_2As_2$ single crystals, Co-doped $BaFe_2As_2$ single crystals, and Co-doped $BaFe_2As_2$ epitaxial thin films. We explored the influence of the irradiation on a variety of properties, including angular-dependent upper critical field (H_{c2}), vortex solid-liquid phase transitions, critical currents, and flux creep. We also investigated the irradiation effects on the superfluid density using the magnetic force microscopy (MFM) technique for the determination of the absolute value of the superconducting penetration depth λ that we had developed previously. We applied the same MFM technique to investigate a single crystal of the recently discovered iron-arsenide superconductor $Ca_{10}(Pt_3As_8)$ $[(Fe_{1-x}Pt_x)_2As_2]_5$, where we found an unusually large λ, and in clean MgB_2 films, where we obtained a consistent description for $\lambda(T)$ and the angular and temperature dependence of H_{c2} using a model for two-band superconductors. Our research during this period resulted in 11 publications, 1 more in press, and 1 more submitted. We presented 4 invited talks at international conferences.

Electronic and Optical Properties of Novel Semiconductors for Energy Applications

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Funding:	$499,000

PROGRAM SCOPE

Advanced energy technologies require high-performance materials, which, in photovoltaics, translates to new semiconductors 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 constraining present photovoltaic and solid-state lighting technologies. It specifically addresses the current unavailability of efficient high bandgap (2.1 eV) and low bandgap (1 eV) absorbers for photovoltaics, and efficient amber emitters for SSL, via technologies based on GaAs substrates. The key to transcending the present limitations is the understanding and control of fundamental electronic and optical processes in semiconductor alloys, which is another goal of this project. Towards this end, the project will focus on understanding the phenomena of spontaneous ordering in high bandgap lattice-mismatched AlxIn1-xP, 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 bipolar Plasmon gasses photogenerated in semiconductors, so as to achieve an understanding of collective phenomena that could enable semiconductors with novel, useful properties. Through collaborative efforts, this project utilizes state-of-the art resources in growth, spectroscopy, and theory, from three national laboratories and two universities, to address the above mentioned issues. By exploiting the use of BES Nanoscience Centers, it brings to bear powerful new tools for the growth and characterization of semiconductors in BES-supported DOE laboratory research.

FY 2012 HIGHLIGHTS

(1) The percolation of impurity states into an electronic band was probed through time resolved and high magnetic field studies to be a disorder-order Anderson transition. We used high magnetic fields (57 T at the NHFML Los Alamos) to expose and study N supercluster states resonant in the conduction band, by quenching the overlap between N cluster states, thus revealing the reverse order-disorder Anderson transition [*Phys. Rev. B (Rapid Comm.)*, 86, 041201 (2012)].

(2) After over three decades of uncertainty about the exact crossover composition x_c for $Ga_xIn_{1-x}P$ alloys, we were able to precisely determine the value of x_c by simultaneously obtaining a spectroscopic signature of the direct and indirect valleys in a region very close to the crossover composition [*J. Appl. Phys.*, 110, 113701 (December 2011)]. This is invaluable for $Ga_xIn_{1-x}P$ applications in multijunction photovoltaics and solid-state lighting.

(3) We showed that the mechanism underlying an unusual asymmetric lineshape broadening observed in Raman spectra on the dilute nitride alloy $GaAs_{1-x}N_x$ was a Fano interaction between the LO phonon and an electronic continuum [*Phys. Rev. B* 86, 045209 (2012)].

Correlated and Complex Materials

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Students:	2 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding:	$2,137,000

PROGRAM SCOPE

The ultimate aim of our research is to attain a predictive understanding of the behavior of correlated and complex materials. This research program will use the experimental tools of materials synthesis, compositional tuning, and crystal growth 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 complex transition-metal compounds. Phenomena such as charge and orbital ordering, coupling of magnetism and ferroelectricity, unconventional superconductivity, low carrier density helimagnetism, and anharmonic phonons in thermoelectric materials are studied. A substantial fraction of the effort will be 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 will be carefully controlled, and the effects of compositional tuning on the basic physics of the materials will be 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 for energy conversion.

FY 2012 HIGHLIGHTS

Research for the past year focused on three topics: (1) the relationship between superconductivity and magnetism in the iron-based superconductors, (2) new mechanisms for enhancing thermoelectric performance, and (3) heat transport by magnetic excitations. We produced the first homogenous crystals of an intercalated iron-selenide, $TlFe_{1.6}Se_2$, and found that the physical properties in inhomogeneous iron-selenide crystals were the result of coupling between ordered and disordered regions. This result has direct implications for the relationship between superconductivity and magnetism in this class of superconductors [May PRL 109, 07703 (2012)]. Many good thermoelectric materials have a large dielectric constant; but does a high dielectric constant help carrier mobility and thermoelectric efficiency? For a class of dopable and tunable ferroelectric crystals ($KTa_{1-x}Nb_xO_3$:Ca), we found that higher carrier mobility did indeed correlate with the dielectric constant. This result also has implications for improving the performance of oxide-based electronics [Siemons Adv. Mater. 24, 3965 (2012)]. For some materials, magnetic excitations can carry significant amounts of heat. In single crystals of the quasi-one dimensional magnet, $CrSb_2$, we were able to show that in the direction of high magnon velocity, the heat transport at room temperature was enhanced by 100%. This result suggests a novel route to designing materials for thermal management applications where heat needs to be guided in one direction [Stone PRL 108, 167202 (2012)].

Interfaces in Epitaxial Complex Oxides

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Funding: $2,010,000

PROGRAM SCOPE

This project addresses the central challenge of creating, understanding, and utilizing interfaces in epitaxial complex oxides 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 to (1) tune functional properties in epitaxially stabilized oxides, (2) manipulate properties that emerge at epitaxial interfaces, and (3) understand the mechanisms of epitaxial interface formation. Underpinning this work is a unique combination of experimental skills, in particular in the growth of perovskites and related materials using pulsed-laser epitaxy, real-time in-situ surface x-ray diffraction monitoring of interface formation, and detailed properties measurements (structure, electronic and ionic transport, magnetism, etc.). Electron microscopy, neutron scattering approaches, and interactions with theory play a key role in all aspects of this work. The resulting enhanced understanding of interface formation, interfacial behaviors, and interfacial effects on complex materials will provide unprecedented guidance in the formation of technologically relevant materials for applications such as energy conversion and storage and will lead to new, highly controlled model systems in which we can explore fundamental physical mechanisms (including correlated-electron behavior, multiferroicity, and coupled electronic and ionic transport).

FY 2012 HIGHLIGHTS

Research efforts in FY 2012 have led to significant advances in the understanding of electronic conduction across junctions in complex oxides and along interfaces in perovskites (including studies of materials where the composition is controlled within a single unit-cell layer). Strain-induced changes of spin order, spin states, and ferroelectric properties have been analyzed in cobaltites and ferrites. Detailed synchrotron studies of epitaxial growth have led to a quantitative determination of energy-enhanced interlayer transport. Finally, the project has led to the identification of mechanisms to tune the band gap and the electronic mobility in complex-oxide materials, as needed for a variety of applications.

Origin of Superconductivity in Structurally-Layered Materials

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Funding: $0.00 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

This project investigates the mechanism of high transition-temperature (T_C) superconductivity by synthesizing promising structurally-layered materials and then characterizing them. The general issues in high T_C 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 the T_C; the development of superconductivity from a normal correlated state; the anisotropic properties of the superconducting and normal states; the identification of the underlying pairing mechanism; the nature of the charge carriers and their role in determining T_C; and the possible interaction between magnetic ions and superconducting charge carriers. The ultimate goal of this proposal is to develop a comprehensive predictive design for superconductors that links the behavior of the cuprates and other structurally layered superconducting materials such as the Fe-based superconductors.

FY 2012 HIGHLIGHTS

Research efforts in FY 2012 have improved our overall knowledge of the underlying physics of correlated materials and possible causes of superconductivity, in several different transition-metal based and structurally-layered materials. Recognizing the important role of layered materials with magnetic fluctuations in producing superconductivity, promising phases were synthesized using chemical reasoning and structure-property relationships. The characterization of these materials was done through basic physical property measurements, neutron scattering experiments, and electronic structure calculations. Such analyses gave information and insight into the structural and magnetic transitions as well as the role of spin fluctuations into the possible superconducting pairing mechanism.

Quantum Tuning of Ultrathin Metal Films for Hydrogen Storage and Enhanced Chemical Reactivity

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Funding: $819,000

PROGRAM SCOPE

The overarching scientific goal of this joint experimental and theoretical research program is to explore and fully exploit the inherently quantum mechanical nature of ultrathin metal films and related hybrid nanostructures for enhanced and tunable chemical performance in hydrogen fuel research. The research theme contains three closely related aspects: (1) establishing the fundamental underpinnings for hydrogen adsorption, dissociation, absorption, diffusion, and recombination on ultrathin metal films and metallic alloys, emphasizing the crucial role of quantum size effects and property tuning; (2) exploring the feasibility of tuning the catalytic properties of ultrathin transition metal systems via size quantization, emphasizing catalytic water splitting reactions for clean hydrogen production; and (3) creating topologically protected surface state systems that catalyze surface chemical reactions, including hydrogen production. These investigations also enrich the fundamental knowledge base towards quantum mechanical design of novel catalytic materials with desired surface chemical reactivity for broader energy applications.

FY 2012 HIGHLIGHTS

Research efforts on the thickness-dependence of surface chemical reactivity of ultrathin metal films have led to the surprise discovery that the surface of an ultrathin epitaxial Ru(0001) film on Pd(111) is far less reactive to oxygen than the surfaces of bulk ruthenium and palladium. This unexpected "noble" behavior of a transition metal thin film seems to be at odds with the venerable d-band model of surface catalysis and may be attributed to quantum size effects and/or formation of a novel surface alloy. In a related effort, we elucidated the origin and nature of the collective plasmon modes of ultrathin magnesium films. We observed a redistribution of oscillator strength between the intersubband plasmon excitations and the semiclassical monopole and multipole surface plasmon modes in a thickness regime where the single-particle states remain fully quantized. The thickness-dependent evolution of the monopole and multipole surface plasmon modes can be correlated semi-quantitatively with the quantum-size-effect-induced oscillations in the decay length of the ground state wavefunctions, suggesting the possibility of engineering the surface plasmon response and plasmonic properties of a thin metal film through the quantum size effect.

Quantum Electronic Phenomena & Structures

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Brueck, Steve, New Mexico, University of
Lee, Mark, Texas, University of
Students: 2 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding: $1,190,000

PROGRAM SCOPE

An important goal of nanoscience is to take novel quantum behaviors occurring at the nanoscale and propagate them upward into the mesoscopic realm. Thus, it is necessary to probe and understand these quantum electronic phenomena not just at the mesoscopic scale, but more deeply at the nanometer scale which is governed by the laws of quantum mechanics.

The focus of this project is to discover, understand, and explain new quantum electronic phenomena, induced by strong electron-electron interactions. The project includes ongoing research in quantum transport studies, electron dynamics, ultrafast optical studies in single nanowires, and high quality nanostructure materials growth. The research presented in this project is at the frontier of the field of condensed matter physics, and contains three topical thrusts that address the issues of what novel types of collective behaviors can emerge from nanostructures and how well this behavior can be controlled and manipulated.

Quantum transport in structured semiconductors: This thrust addresses quantum transport properties in top-down fabricated nanostructures. We search for and examine novel many-particle quantum phenomena, including non-Abelian statistics, quantum spin Hall effect, topological superconductor, quantum coherence and phase transitions, Bloch oscillations, electron tunneling in 1- and 0-dimensional structures, Coulomb drag, relationship between high mobility 2D electron systems and the geometry of the dopants that form the 2D electron system, and individual quasiparticles in quantum Hall systems.

Growth and properties of III-nitride and III-V nanowires: The focus of this thrust is to synthesize novel, high quality nanostructures that may exhibit exciting quantum electronic properties. One activity will be to investigate spin-orbit coupling in III-nitride nanowires using electronic and optical methods. Time resolved ultra-fast optical measurements are also utilized to examine the collective electron excitation modes and surface states in these nanostructures.

Electron Dynamics of Low Dimensional Quantum Systems: The focus of this task will be to apply high frequency (microwave to terahertz) and time-resolved (picosecond to nanosecond) methods to provide a direct window into unconventional charge transport and scattering mechanisms, elementary excitation spectra, and correlation strengths in low dimensional and nano-structured quantum systems of the type currently being studied by DC methods in the above two tasks.

FY 2012 HIGHLIGHTS

Exciting results obtained from this project include the following: (1) A surprising spin transition is observed in the 8/3 fractional quantum Hall effect. (2) New features were observed in Coulomb drag signals in vertically coupled double quantum wire system. (3) Spatial distribution of defect luminescence was achieved in GaN nanowires. (4) For the first time, we demonstrated coherent coupling between adjacent plasmon cavities by using specially designed devices to antenna couple THz radiation into microscale 2DEG structures.

Atomic Engineering Oxide Heterostructures: Materials by Design

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Funding:	$500,000

PROGRAM SCOPE

This program focuses on developing the science and technology of interfaces between transition metal oxides. In the search for emergent phenomena and ever higher functionality in devices, transition metal oxides have significant potential since they host a vast array of properties, such as orbital ordering, high temperature (and unconventional) superconductivity, ‘colossal’ magnetoresistance, all forms of magnetic ordering and ferro¬electricity, as well as (quantum) phase transitions and couplings between these states. Using atomic scale growth techniques, we explore the synthesis of novel interface phases, with a current emphasis on polar surface doping of quantum wells and control of interface dipole formation. X-ray probes are used to determine the static and dynamic electronic and magnetic structure in ultrathin films and superlattices. Heterostructures with low-density superconductors are used to explore new experimental regimes of low-dimensional superconductivity, particularly in the presence of tunable pinorbit coupling and disorder. Together, these activities address the newly-revealed experimental opportunities enabled by atomically controlled growth of complex oxide heterostructures, and develop the fundamental design principles which underlie the creation of new electronic, magnetic, and superconducting states for science and technology.

FY 2012 HIGHLIGHTS

Highlights of FY 2012 include the following:

(1) LaAlO3/SrTiO3: Following the initial scanning SQUID observation of magnetism at the LaAlO3/SrTiO3 interface, significant progress has been made in determining a critical LaAlO3 thickness for the onset of magnetism, transport studies of the spin-orbit coupling, and XMCD studies which provide the first spectroscopic determination of the magnetic structure.

(2) Engineering interface dipoles: These studies initiated in FY 2011 have been nearly completed, with the demonstration of tuning band alignments in excess of 1.7 eV by the insertion of interface charge layers (with dipole completion via induced screening charge) and by the insertion of insulating dipole layers via polar perovskites.

(3) Delta-doping SrTiO3: A study of the spin-orbit coupling derived from normal state and superconducting state magnetotransport has quantified the coupling strength via localization and upper critical field measurements.

(4) Anatase/perovskite heterointerfaces: We have completed the initial study demonstrating the ability to tune high mobility interface conductivity by control of the termination layer at the interface. These results are promising for new approaches to transparent conducting devices, and for combining with other SIMES efforts in pursuit of their catalytic function.

Spin Physics

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Funding:	$415,000

PROGRAM SCOPE

The Spin Physics program investigates novel phenomena arising from spin-orbit coupling in solids. In conventional semiconductors, spin-orbit coupling gives the possibility of electric manipulation of the spin degrees of freedom, which can be used for data storage and information processing. More recently, it is 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 2012 HIGHLIGHTS

Our theory group has successfully predicted 2D and 3D topological insulators in HgTe and Bi2Te3 systems. In these systems, spin-orbit coupling of the heavy elements play a dominant role, and the interaction effects can be neglected. The field is now focused on topological Mott insulators, where the interactions play a crucial role. We proposed that the actinide materials PuTe and AmN could be topological Mott insulators, only when interaction effects are take into account [Science 335, 1464 (2012)]. If confirmed, this would be the first interacting topological insulator observed in Nature. Our theory group also actively works on theoretical predictions on novel effects of topological insulators, including the topological p-n junction, the quasi-particle interference on the surface of TI, and helical modes on the surface of weak Tis. The Orenstein group made significant progress in understanding the fundamentals of spin dynamics in spin-orbit coupled electron gases [Phys. Rev. Lett. 106, 247401 (2011); Nature Physics 8, 153-157 (2012).] The Manoharan group made significant progress this year in STM/STS and atomic manipulation studies of new quantum materials and spin/pseudospin-based topological ground states, including the first “designer” Dirac fermions synthesized by transforming normal surface states on Cu(111) into hosts for massless Dirac fermions [Nature 483, 306–310 (2012); Physics Today 65, 76 (2012)]. Goldhaber-Gordon's group has also been developing a novel probe of electron organization in buried 2D electron systems, which serve as clean, tunable models for correlated electron behavior [Appl. Phys. Lett. 97, 132103 (2010)].

Materials Chemistry

Institutions Receiving Grants

Quantum Dot and Quantum Wire Solids

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Funding: $165,000

A summary for this program was not available at press time.

Activation of Hydrogen under Ambient Conditions and Unusual Element Hydride Reactivity by Main Group Molecules

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Funding: $170,000

PROGRAM SCOPE

The main objectives of our research are the investigation of the reactions under mild conditions (25°C, one atmosphere of pressure) of hydrogen and related molecules with a range of heavier (principal quantum number $n \geq 3$) main group species having strained geometry (i.e., bent or pyramidalized) in comparison to their lighter (principal quantum number $n = 2$) congeners and the understanding of the mechanism whereby these reactions proceed. The geometries in the heavier element complexes resemble and represent molecular models for the geometries of the atoms at the exposed surfaces of elements such as silicon and germanium, which display high reactivity. The reactive main group species are characterized by frontier orbitals that have relatively low energy separations and are usually of the correct symmetry to interact with small molecules.

The ultimate goals of this work are the achievement of reversibility in the absorption and release of small molecules and their activation, as well as the application of such reversible reactions to the development of catalysts based on earth abundant elements such as silicon or aluminum.

FY 2012 HIGHLIGHTS

A major focus has been on the room temperature activation of C-H bonds by main group element compounds. We have shown that two separate classes of germanium compounds can activate C-H bonds in cyclic alkenes and isocyanides at 25°C. In addition, we have shown that compounds of the element gallium can undergo reversible and irreversible cycloaddition reactions with polyolefins and have rationalized these reactions with the assistance of density functional calculations. We have also determined the mechanism whereby hydrazine adds to low valent germanium compounds at room temperature and shown that such insertions are heavily dependent on steric factors.

Unconventional Clathrates Based on Transition Metal Pnictides: A Paradigm-Shifting Approach to Materials with Enhanced Thermoelectric Properties

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Funding:	$150,000

PROGRAM SCOPE

Thermoelectrics convert heat into electric energy and vice versa and as such are promising materials for the waste heat reduction or recovery, thus enhancing energy efficiency and diminishing our dependence on fossil fuels. Development of novel materials where charge and heat transport are partially de-coupled is a key factor for the next generation of thermoelectrics. This project seeks to develop a new class of bulk thermoelectric materials with record-breaking characteristics. Although much current research emphasizes nanocomposites, their increase in thermoelectric efficiency is only 10-20% over that for the parent bulk materials. Thus, if significant breakthroughs in the area of thermoelectrics materials are to be achieved, new classes of bulk materials need to be discovered. Materials where charge and heat transport are de-coupled will be found among semiconducting Zintl clathrates with a host-guest type of structure. In their crystal structure, guest cations are encapsulated in the oversized polyhedral cages of the three-dimensional host framework based on a tetrel, group 14 elements: Si, Ge, or Sn. Rattling of guest cations provide effective scattering of heat carrying phonons while host framework is responsible for charge carriers transport. Relatively large band gaps and low density of states in the vicinity of Fermi level are main reasons for moderate thermoelectric efficiency of conventional Zintl clathrates. A clathrate containing *d*-metal in the framework together with *f*-element guest ions in the cages will not suffer from these drawbacks. Frameworks of conventional clathrates based on group 14 elements are able to accommodate very small amounts of transition metals and essentially no small rare-earth Ln^{3+} guest cations. This project is devoted to the development of novel thermoelectric materials based on tetrel-free (without group 14 elements) clathrate compounds with *d*- and *f*-elements. Extensive metrology will be used to characterize crystal and electronic structures of new compounds. Thermoelectric properties of novel clathrate phases will be studied in a wide temperature range (2–1000 K).

FY 2012 HIGHLIGHTS

Project start date: September 01, 2012. Thus far, we have successfully synthesized and structurally characterize two new transition metal clathrate compounds. Preliminary thermoelectric properties measurements indicate that these tetrel-free clathrates exhibit ultra-low thermal conductivity of <0.6 W/K·m in the temperature range of 2–300 K. Further work will include optimization of the charge carrier concentration to improve the power factor of new materials.

Optical Spectroscopy and Scanning Tunneling Microscopy Studies of Molecular Adsorbates and Anisotropic Ultrathin Films

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Funding:	$162,000

PROGRAM SCOPE

The emphasis of our research is to develop sufficient fundamental understanding to allow the controlled preparation of nano-structured ultrathin films with novel optical properties and chemical reactivity. The research places an emphasis on the impact of ordering phenomena on the molecular and mesoscopic scale on surface properties of materials. In this research, we combine the use of optical probes (polarization and angle-dependent laser reflectivity and laser Raman scattering, and laser-induced desorption coupled with Fourier transform mass spectrometry) with modern surface imaging experiments (electron microscopy and variable temperature ultra high vacuum scanning tunneling microscopy). These experiments are combined with conventional methods of UHV surface science (high resolution electron energy loss vibrational spectroscopy, Auger electron spectroscopy, x-ray photoelectron spectroscopy, and thermal desorption spectroscopy). The conventional surface probes provide well-tested methods for the preparation and characterization of substrates. The optical probes used in our experiments provide powerful methods for the characterization of the structure-dependent optical properties of novel molecular and nanometer scale surface structures as well as molecular identification and quantification of adsorbates in monolayers and ultrathin films. The emphasis of our research is on the generation of novel nanometer scale morphologies and the resultant optical and chemical reactivity properties. These experiments will involve more complex molecular adsorbates, which we are well equipped to study using techniques in our laboratory.

FY 2012 HIGHLIGHTS

We have made progress in three areas of this project. (1) We have successfully obtained high resolution electron energy loss vibrational spectra of hydrocarbons adsorbed onto Pt nanoparticles that are supported on ultrathin films of aluminum oxide. In these experiments, our results show that the chemistry of cyclohexane on supported Pt nanoparticles differs from that observed on the low index Pt(111) surface, rather it resembles more the chemistry observed on the corrugated (1x1) Pt(110) surface. (2) We have successfully developed methods to prepare aluminum oxide ultrathin films on NiAl that are sufficiently flat to image by STM. These surfaces will be used to image the chemistry of hydrocarbons on Pt nanoparticles on the oxide surfaces. (3) We developed photoelectrochemical approaches to the deposition of transition metal nanoparticles onto highly characterized titantium dioxide nanoparticles. We have carried out detailed studies of the photoelectrochemical deposition process and have elucidated the electrochemical reactions processes involved.

Rational Design and Nanoscale Integration of Multi-Heterostructures as Highly Efficient Photocatalysts

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Sr. Investigator(s):	
Students:	0 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$150,000

PROGRAM SCOPE

The central goal of this project is to rationally design and synthesize a new generation of highly complex multi-hetero-nanostructures and fundamental investigation of their potential as efficient and robust photocatalysts. Specifically, the project aims to integrate a nanoscale semiconductor photodiode (photovoltaic device) as the light harvesting antenna with two distinct redox nanocatalysts in a single multi-hetero-nanostructure. In this heterostructure, photoexcitation creates electron-hole pairs that are quickly separated and directed towards the integrated nanocatalysts to drive thermodynamically uphill redox reactions and directly convert solar energy into chemical energy *on site*. Systematic studies will be carried out to develop general strategies for the synthesis of such complex nanostructures, and to investigate their fundamental electronic, optical, and photocatalytic properties. The specific scopes of this project include (1) the design and synthesis of highly complex nanostructured semiconductor photodiodes with desired built-in potential through a precise control of chemical composition, physical size, and the multi-hetero-structure architecture; (2) the investigation of their fundamental electronic, optoelectronic properties, and optimize the material interface for efficient charge separation, transportation, and photon-to-electron conversion; (3) the development of rational chemistry to integrate the photodiodes with effective redox nanocatalysts to facilitate the interface charge transfer in photocatalytic reactions; and (4) the investigation of such multi-hetero-nanostructures as highly efficient photocatalysts for important photocatalytic reactions such as water splitting or CO_2 reduction reactions.

FY 2012 HIGHLIGHTS

We have demonstrated a proof-of-concept Pt/n-Si/n^+-Si/Ag multi-heterostructure to exhibit highly active photocatalytic properties. Additionally, we have demonstrated integration of such heterostructures with plasmonic nanostructures for further enhancement of the photocatalytic properties. We are currently investigating the integration of such heterostructures with graphene and other molecular catalysts to further improve their stability and activity. We are also setting up a metal-organic chemical vapor deposition system for the growth of large band gap (e.g., InGaN) heterostructures for this purpose.

Solid State Electronic Structure and Properties of Neutral Carbon-Based Radicals

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Funding: $242,000

PROGRAM SCOPE

The goals of our work are the synthesis and characterization of a new class of organic molecular metals and superconductors based on neutral carbon-based spin = ½ radicals, and the application of these materials in new electronic and photonic devices such as organic photovoltaic (OPV) solar cells. The molecules are synthesized by the methods of organic chemistry, converted to salts, and then reduced in solution to give the carbon-based radicals the form of powders or crystals. We characterize the solid state properties by optical, magnetic, and conductivity studies and, where appropriate, by incorporation of the materials into device structures. Our current molecular family of choice is the spiro-biphenalenyls, 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. Our target radicals are designed to optimize the solid state transport properties of the phenalenyl radicals, either by increasing the bandwidth (W), or reducing the energy of an ionic fluctuation (effective on-site Coulomb repulsion, U). Thus we propose to introduce chalcogenide substituents into the phenalenyl systems so as to minimize U while increasing W due to the presence of extended intermolecular solid state interactions between the phenalenyl units.

In the current funding period, we investigated the effect of increasing the bandwidth (W) in structures involving the π-chain stacking motif by preparing derivatives of the benzophenalenyl (BPLY) system, the simplest π-extended derivative of phenalenyl; and we crystallized and characterized spiro-bis-benzophenalenyl radicals. In FY 2012 we further developed this theme and focused on the design and synthesis of extended π-electron derivatives of triangular phenalenyl units, such as naphthophenalenyl (NPLY) and the introduction of chalcogenides. The study of these extended phenalenyl systems should further improve the solid state transport properties and lead to a better understanding of the intriguing electronic and magnetic properties of nanographene; and the stability of the spiro-biphenalenyl structures offers a route to large, isolable open shell graphitic structures which can be characterized and studied in the solid state.

FY 2012 HIGHLIGHTS

We devised a method to introduce chalcogenide substituents into the phenalenyl ring system; and we synthesized and characterized a series of (1) tetra-alkylthio spiro-bis-phenalenyl radicals, (2) tetra-thio and -seleno bridged spiro-bis-phenalenyl radical precursors, (3) thiocarbonate bridged spiro-bis-phenalenyl radical precursors, and (4) the hexathiophenalenyl radical precursors. We developed synthetic routes for the preparation of highly condensed PLY structures such as naphthylated phenalenyl and were able to characterize the first spiro-bis-naphthophenalenyl radical. In the next period, our focus will be on synthesis and crystallization of the radicals from these novel precursor compounds.

Tuning Sorption Properties of Metal-Organic Frameworks via Postsynthetic Covalent Modification

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Students:	2 Postdoctoral Fellow(s), 1 Graduate(s), 2 Undergraduate(s)
Funding:	$220,000

PROGRAM SCOPE

The overall goal of this program is the development of functionalized metal-organic frameworks (MOFs) for use in various energy-related gas sorption applications. MOFs combine organic ligands and metal ions to generate porous, crystalline materials with defined topologies. The primary strategy for obtaining functionalized MOFs, which differentiates this program from most others, is the use of postsynthetic methods to introduce functionalization into these materials. Postsynthetic methods such as postsynthetic modification (PSM), postsynthetic deprotection (PSD), and postsynthetic exchange (PSE, recently discovered during the course of the studies for this program) make up our primary techniques. Collaborative studies with analytical chemists (Kim Prather, UCSD), computational chemists (Francesco Paesani, UCSD), and chemical engineers (Krista Walton, Georgia Tech) have enhanced our ability to characterize and understand the properties of functionalized MOFs. We have successfully achieved many of the goals, with respect to PSM, outlined in our original proposal and have discovered many additional avenues of related research. Our recent efforts have focused on three main areas: (1) the use of PSM to obtain novel functionalized MOFs, (2) the discovery and development of postsynthetic exchange (PSE) as a functionalization approach to MOFs, and (3) the preparation of self-assembled supramolecular clusters based on phosphines and coinage metals.

FY 2012 HIGHLIGHTS

To date, we have made a wide variety of functionalized MOFs, including both bifunctional and cyclometalated species (both described as primary goals in our original proposal). Bifunctional MOFs, containing two organic functionalities on a single ligand, were found to have very unique gas sorption and breathing behavior. With respect to cyclometalated MOFs, we have successfully designed and synthesized an organic linker that contains two different metal binding moieties. One moiety is used for the construction of MOFs, and the other one can be used to immobilize a reactive organometallic species ($[Ir(COD)(OCH_3)]_2$ or $[Rh(COD)(Cl)]_2$). In the course of our studies on MOF modification, we discovered PSE, where functionalized ligands can be introduced into MOFs via a dynamic ligand exchange process. This new tool has the power to make unique MOFs that cannot be accessed by traditional synthetic approaches or PSM. Finally, we have discovered a new class of supramolecular metal-phosphine clusters formed from tritopic/ditopic phosphines and coinage metals. This work developed out of studies of MOFs and may serve as the basis for new cluster compounds for the storage and separation of gases. Future studies will focus on the gas-sorption and host-guest behavior of these materials, as well as the investigation of other supramolecular clusters using non-coinage metals.

Charge Recombination, Transport Dynamics, and Interfacial Effects in Organic Solar Cells

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Wudl, Fred, California-Santa Barbara, University of
Students: 7 Postdoctoral Fellow(s), 4 Graduate(s), 1 Undergraduate(s)
Funding: $600,000

PROGRAM SCOPE

The objective of this proposal is to take advantage of new device strategies, function-specific materials, and interfacial phenomena to improve the performance (open circuit voltage, short circuit current, fill-factor, and power conversion efficiency) of polymer-based photovoltaic devices fabricated by processing all layers from solution. Fundamental understanding of charge generation, transport, and recombination dynamics in thin film bulk heterojunction (BHJ) polymer:fullerene blends and in solar cells made from such BHJ blends will be studied using transient photoconductivity and impedance spectroscopy. Light intensity and temperature-dependent current-voltage measurements will reveal the charge recombination kinetics. Devices utilizing conjugated polyelectrolyte and oligoelectrolyte interlayers to improve open-circuit voltage and fill factor will be explored with an emphasis on establishing a deeper understanding of the working mechanism. New conjugated polyelectrolytes and oligoelectrolytes will be synthesized and their functions as interlayers in BHJ solar cells will be investigated. Sensitive probes and experimental methods that enable detailed characterization of the interfaces, the local molecular organization, and the charge generation at the nanoscale will provide details of the structure/property relationships across multiple length scales. The combined and synergistic multidisciplinary approach will demonstrate the feasibility of stable, efficient solar cells that can be manufactured using printing and coating technology as a route to low-cost solar energy conversion.

Relationships between the Adhesion, Friction and Nano/Micro-Structure of Materials, Surfaces and Films

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Funding: $282,000

PROGRAM SCOPE

The program aims are to apply recently developed experimental techniques, and develop new ones, for making simultaneous static and dynamic measurements of adhesion, friction, structure, and wear of both model and ‘engineering’ surfaces and materials, i.e., surfaces and materials of both fundamental and practical interest. The project involves modifications and new attachments to the Surface Forces Apparatus (SFA) allowing for simultaneous measurements of interaction forces and other physical properties, such as electric field effects and real time imaging of the accompanying changes in the nano- and micro-structures of the surfaces and thin films, and—most recently—electrochemical reactions at and between two closely apposed surfaces in electrolyte solutions.

FY 2012 HIGHLIGHTS

Development and first applications of the “electro-chemical SFA” for simultaneous measurements of interaction forces and electrochemical reactions: The electrochemical surface forces apparatus (EC-SFA) is a significant extension to the traditional SFA technique which now allows measurement and/or control of the electrochemical potentials of surfaces in-situ. The EC-SFA contains all of the advantages of the traditional SFA technique, including the same force and distance resolutions. In 2011-2012 the EC-SFA was used to measure (1) the friction forces at a metal-ceramic contact and their dependence on the applied electrochemical potential, (2) the chemical identification and changing thickness of anodically-growing oxide layers with angstrom-level accuracy on both smooth and rough surfaces, and (3) the electrochemical dissolution of silica, with implications for better understanding the phenomena of Pressure Solution, Chemical Mechanical Polishing (CMP), and corrosion. All of these measurements were successfully rationalized and quantitatively modeled in terms of established colloidal theories and electrochemical reaction equations, thus confirming the reliability of this novel multi-modal experimental technique.

Designing wearless lubricant systems: We have found a way to design lubricant molecules and surfaces where the surfaces never stop moving during a reversal, thereby eliminating one of the most common causes of wear of materials. Using a modified “3D-SFA” that can apply and measure forces and motion in all three directions in space, we measured the friction forces generated by nano-thin liquid films of linear hydrocarbon chain molecules between two mica surfaces whose crystalline surface lattices could be oriented at different ‘twist angles’, and where the moving surface was allowed to move off-axis during back-and-forth sliding. The anisotropic lubricant molecules and anisotropic surface lattices (nano structure) resulted in ‘anisotropic friction forces’ and a complex path taken by the surfaces manifested by a non-zero ‘off-axis’ velocity at all stages of back-and-forth sliding, and absence of damage even after prolonged shearing. These findings should enable engineers to design systems that resist stiction—the momentary high levels of friction that occur in a wide range of mechanical devices where sliding surfaces are subject to repeated back-and-forth motions.

Nanoscopic Control of Liquid Crystal Orientation via Atomic Force Microscope Writing of Substrates

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Funding:	$132,258

PROGRAM SCOPE

The primary goals of this project are to (1) manipulate substrates on nanoscopic length scales in order to control liquid crystalline order, (2) optically image the liquid crystalline order on nanoscopic length scales, and (3) control and investigate induced chiral behavior, which often occurs on length scales of a few nanometers. Projects (1) and (2) are naturally complementary. We scribe patterns on polymer-coated substrates that serve as an orientational template for liquid crystal molecules and, in the process, elicit new physical phenomena. We then apply our technique of optical nanotomography in which we immerse a highly tapered optical fiber into the liquid crystal layer and create three-dimensional images of the order with volumetric resolution 500 times better than confocal microscopy. A particularly rich application of our approach involves the creation of chiral nanopatterns, such as steps and spirals, on surface, which induce chiral behavior by means of conformational deracemization in a configurationally achiral liquid crystal in contact with the surface. The (related) central question we wish to address is *How is chirality induced and over what length scale does chiral induction occur?* To that end we also are investigating surfaces of chiral carbon nanotubes ("CNTs") and periodic mesoporous organosilica ("PMO") colloids, which we also have shown induce chirality into a surrounding liquid crystal. By examining topological defects, performing optical nanotomography of the CNTs and PMO colloids in situ, and electrooptical measurements, we are developing a picture of chiral induction at surfaces. More recently we have branched out, studying the effects of ferroelectric and ferromagnetic nanoparticles ("NPs") on liquid crystal order, especially at and near surfaces. Here we are doping nanopatterned alignment layers, such as polyimides, with the NPs to examine how the (primarily anisotropic dispersive and Coulombic) interactions between alignment layer and liquid crystal can be altered by field-responsive NPs. The impact of our work will be an improved understanding of surface interactions and an ability to manipulate by patterning and doping surfaces to provide desired responses.

FY 2012 HIGHLIGHTS

We have demonstrated that a step-pattern scribed on a polymer surface is chiral and can induce chirality into the adjacent liquid crystal. In particular, we have explained how and why the chirality strength can be controlled by varying the step height-to-width ratio. We also have examined the propagation of chirality from inside the pores of PMO colloids into the surrounding achiral fluid and demonstrated that CNTs induce a chiral electrooptic signature in the surrounding liquid crystal, using the time dependence of this signature to obtain an—at this time crude—estimate of the chiral induction length.

Towards Molecular Engineering of Polymer Glasses

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Funding:	$175,000

PROGRAM SCOPE

We recognize several essential thrust areas where the guidance of our molecularly oriented theory of glass-formation will strongly impact the design of cutting edge glassy polymer materials. First, we plan to continue our studies of how monomer molecular structure and interactions affect the properties of glass-forming polymers by investigating the dependence of the glass transition temperature and fragility of polymer melts on side chain branching. Since many glassy materials are polymer blends or involve nano-particles dispersed in blends, we will extend our theory to describe the coupling between phase separation and glass-formation in two- and multi-component polymer mixtures. Another important class of polymer materials becomes glassy because of the presence of associating groups (e.g., hydrogen bonding, charged groups in polyelectrolytes, etc.). Our proposed project to describe how polymer association and self-assembly broadly alter the nature of polymer glass-formation will be essential to guide the design of this type of new materials. We have unique expertise in developing a systematic theory of supramolecular assembly within a Flory-Huggins statistical mechanical framework, so merging the molecular theory for strongly interacting systems and our theoretical methods for the description of glass-formation in polymer melts represents a logical synergy. However, the requisite theory is extremely complex, and we will therefore investigate approximate treatments that are more tractable to devise simpler, but accurate alternatives. We plan to interact with Sokolov (ORNL) and other experimentalists to help steer our efforts in directions that will impact their research and aid in the design of new materials.

FY 2012 HIGHLIGHTS

During the first month of the grant period, we have been considering applications for a postdoctoral researcher to work on the project (arrival expected around the beginning of January 2013). We have begun developing computer codes to study the influence of side chain branching on the glass transition temperature and the fragility of single component polymer glass-formers. Work is beginning on the more difficult problem of describing the properties of glass-forming polymer blends, especially when the systems are phase separated (with either lower or upper critical solution phase diagrams). Work has been initiated on devising the theory and the corresponding computer codes for describing multi-component glass-forming polymer mixtures.

RECOVERY ACT - Theory and Simulation of Tailored Assembly in Rod-Coil Polymer Nanocomposite

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

PROGRAM SCOPE

The overarching goal of this project is to computationally design and engineer conjugated polymer based nanocomposites for improved efficiency in organic photovoltaic (OPV) devices. Specifically, we are studying morphology within conjugated polymer nanocomposites consisting of nanoadditives and a conjugated polymer matrix, using an integrated approach of theory and molecular simulations. It is well accepted that the efficiency of OPV devices is directly related to charge transport and exciton separation or recombination occurring in the active layer containing electron donor and acceptor materials. For efficient charge separation and transport, there is a need for interfaces between donor and acceptors, continuous pathways through donor and acceptor domains, and domain widths of the order of 10 nm to avoid exciton decay. Thus, the morphology within the active layer plays an important role in the device efficiency. This motivates us to study computationally how design parameters at the molecular level of the donor polymers and acceptor molecules affect their assembly into morphologies in the active layer, providing guidelines for how to achieve optimal morphologies for high efficiency devices. In this regard, we are conducting theory and simulation studies of three systems: (1) blends of conjugated polymers (donor) and bare additives (acceptor), (2) rod-coil polymers and nanoadditives, and (3) blends of polymer grafted particles (donor-acceptor) and free polymer (acceptor).

FY 2012 HIGHLIGHTS

Our works focusing on blends of polymer grafted particles (donor-acceptor) and free polymer (acceptor), and blends of conjugated polymers (donor) and bare additives (acceptor) have been accepted for publication in *Physical Review Letters* and *Journal of Polymer Science B Polymer Physics*, respectively. The *Phys. Rev. Lett*. paper presents our theoretical predictions that when nanoadditives (acceptor molecules) are grafted with polydisperse polymers, the nanocomposite is driven towards a morphology where the dispersion of additives in the free polymer is stabilized. In the paper accepted in *J Poly Sci B: Poly Phys*, we present our recent Langevin dynamics study showing effects of polymer architecture (e.g., side chains, backbone flexibility of oligomers) and the pair-wise interactions between the constituents of the polymer-acceptor blends on the blend morphology and phase transition.

Measuring the Importance of Valence to Chemistry of Nanocrystal Surfaces

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PROGRAM SCOPE

The goals of this project are 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 seek 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) Using this information, 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. NMR spectroscopy is a powerful tool to monitor ligand binding and determine binding constants, exchange rates, and exchange mechanisms. By exchanging anionic organic ligands with a monolayer of halide ligands, we are fabricating nanocrystal thin-films to study charge recombination and transport within closely coupled nanocrystal solids. Electrical conductivity in these films is dramatically enhanced upon forming close internanocrystal contacts because electrical carriers can delocalize into neighboring nanocrystals. Our goal is to evaluate the role of the metal-halide passivation layer on the magnitude of internanocrystal coupling, grain growth during film sintering as well as the concentration and the depth of charge trap states within the nanocrystal solid.

FY 2012 HIGHLIGHTS

We have developed a technique to exchange nanocrystal surface ligands for a surface monolayer of metal-halide and phosphine or amine ligands. These chloride-terminated CdSe nanocrystals are soluble in organic solution and are readily deposited into thin films. Field effect mobility measurements on these films show high electron mobilities (13 $cm^2 V^{-1} sec^{-1}$).

Synthesis, Characterization and Properties of Nanoparticles of Intermetallic Compounds

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Funding: $270,000

PROGRAM SCOPE

The adoption of fuel cell technologies, especially those based on polymer electrolyte membranes and that operate near room temperature, has been stymied due to the need for more durable and less expensive materials in the heart of the fuel cell, the membrane electrode assembly. In particular, the catalysts used in the electrodes need considerable improvement.

There are a number of research groups searching for new catalysts using combinatorial thin film techniques. When potentially useful compositions are discovered, it will be necessary to prepare uniform nanoparticles all having the same composition and structure for use in real fuel cells. To address this need, this project focuses on developing a general synthetic procedure to prepare nanoparticles of intermetallic compounds containing up to four elements from groups III through XV in the periodic table.

FY 2012 HIGHLIGHTS

We have now developed a broadly applicable method to prepare binary intermetallic nanoparticles and to disperse them onto suitable catalyst supports. In this approach, tetrahydrofuran (THF) is used as a solvent for the dissolution of metal chlorides or lithium metal chlorides that are then reduced by alkali metal alkylborohydrides. In most cases, the amorphous or alloy nanoparticles of the dissolved metals are encapsulated in a matrix of a KCl by-product that allows the particles to be annealed at temperatures up to 650 °C without significant growth in particle size. At the same time, structural ordering can often be induced by such annealing. Finally, the nanoparticles can be transferred to catalyst supports by dissolving away the KCl in ethylene glycol, which also prevents agglomeration of the nanoparticles while being released from the KCl matrix. Annealing often also enables intermetallic order to develop, usually when such ordering is expected from the bulk phase diagram.

We are now exploring the details of nanoparticle nucleation and growth of individual compositions across the periodic table that have already been shown to have some promise in different combinatorial searches, determining the difference in catalytic and corrosion behavior between alloys and ordered phases of the same composition, and extending the studies to ternary and even quaternary compositions. The general procedure for binary phases has now been published.

Novel Pnictides with d- and f- Metals as Prospective Materials for Thermal Energy Conversion

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Funding:	$180,000

PROGRAM SCOPE

Using rationally designed syntheses, we propose a plan to seek new bulk materials for applications in solid-state energy conversion. We will undertake thorough and systematic studies focused on the development of the fundamental chemistry and physics of such compounds at the borderline between the typical metals and the typical semiconductors (aka Zintl phases). Our studies will identify new intermetallic compounds that are based on the metals from group I and II together with the metals of the lanthanide series, the transition metals with half-filled or completely filled shells, and the group 15 elements—P, As, Sb, and Bi (aka pnictogens). Ultimately, the derived structure-property relationships (established on the basis of collaborative 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 will be the initial part of a broader interdisciplinary program to investigate the structure-property relationships in a wider variety of lanthanide-based intermetallics with useful magnetic, electronic, and transport properties. We are confident that better understanding the relationship between the composition, structure, electronic structure, and physical properties will be crucial for the development of new materials and technologies for thermoelectric applications.

This proposal is aligned with the DOE-BES missions for reliable and clean energy, as well as with the programmatic focus of the Materials Chemistry program to foster activities along the lines of synthesis of new materials. The anticipated far-reaching outcome of our research supports the DOE missions in new, fundamental knowledge on alternative energy technologies and cleaner environment. Such an energy research initiative will also have an immediate impact for the University of Delaware: (1) The proposed studies will cut across the traditional boundaries of the physical science, encompassing chemistry and physics, and will give excellent training in solid-state chemistry and advanced physical techniques for the characterization of solid compounds to graduate and undergraduate students. This will allow them to be more competitive on the global job market by going on to various careers and actively contributing to the U.S. scientific progress. (2) These studies will initiate an active collaborative program at the University of Delaware to further search for novel phenomena and to deepen our understanding of how and why specific atomic interactions determine the transport and electronic properties of a given compound. These activities may lead to technology-transfer opportunities and to the development of practically useful concepts. (3) Finally, our fast-paced program will bring new research and educational capabilities. All of the above will enhance the vitality of other Departmental programs as a whole and will advance the group research to ensure vigorous and sustainable research programs in solid-state chemistry and physics in the future.

Low Temperature Synthesis of Carbide-Derived-Carbons from Binary and Ternary Carbides in the Si-Ti-C System

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Funding: $150,000

PROGRAM SCOPE

The goal of this project is to investigate the formation of carbide-derived carbon (CDC) from binary and ternary carbides in the Ti-Si-C system (i.e., TiC, SiC and Ti_3SiC_2) with the focus on synthesis at moderate temperatures compatible with electronic manufacturing. Our research will address CDC formation and structural evolution. We have chosen the Ti-Si-C system for several reasons. First, carbides from this system were shown to yield CDC materials with tunable porosity at higher temperatures. The chosen carbides are widely used; and high-purity materials can be purchased from various suppliers as nanopowders, micropowders, whiskers, single-crystals, and thin films. More importantly, the different bonding strength between the metal and carbon atoms in these carbides allows us to investigate possible limitations of low-temperature CDC formation and strategies to overcome them. When CDC formation is limited by the presence of a native oxide scale (e.g., silica), removal of that oxide will enable carbon formation. Parametric studies on sample pre-treatment will elucidate this aspect. Various analytical tools (Raman spectroscopy, electron microscopy, and XPS) will be used to characterize the carbon structure. Pore size distributions and pore volume will be measured by gas adsorption. Cyclic voltammetry and electrochemical impedance spectroscopy will be used for electrochemical characterization. This project will address low-temperature chlorination as a way to produce CDC materials for applications in the fields of gas and energy storage, once the basic principles and limitation of CDC formation are understood. Until now, the lack of systematic basic science studies greatly limits CDC applications.

FY 2012 HIGHLIGHTS

We synthesized CDC films on SiC and TiC, produced CDC nanopowders, and manufactured electrochemical micro-capacitors with interdigital electrodes and studied their electrochemical performance. Future efforts will focus on understanding the effect of thermal annealing on carbon structure and electrical and electrochemical properties. Also, room temperature synthesis of CDC films will be attempted.

Luminescence in Conjugated Molecular Materials under Sub-Bandgap Excitations

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PROGRAM SCOPE

In a light-emitting diode, light emission is not normally observed until the applied voltage reaches the bandgap voltage of the semiconductor. However, we have previously demonstrated that an organic light emitting diode can be turned on at a voltage below its bandgap voltage when ZnO nanoparticles (NPs) are used as the electron transport layer. This sub-bandgap turn-on voltage is attributed to an Auger-assisted energy up-conversion process at the polymer/ZnO NP hetero-interface. For example, the energy released from the non-radiative recombination of a hole in the polymer HOMO and an electron in the ZnO NP conduction band is transferred to an Auger electron in ZnO so that it has sufficiently high energy to inject into the LUMO level of the polymer. The efficiency of the energy up-conversion process depends strongly on the nature of ZnO NPs. For example, the lowest turn-on voltage was observed in devices employing 2~3 nm size ZnO NPs. The objective of this present work is to understand the electronic structure of these ZnO nanostructures and how they affect the carrier dynamics. Here, we studied the properties of both colloidal ZnO NPs and sol-gel ZnO nano-clusters, and determined how surface treatment affects their electronic properties and the resulting devices.

FY 2012 HIGHLIGHTS

Colloidal ZnO NPs are known to have up to 30% of the atomic bonds dangling, and these defects give rise to a high density of recombination centers. In order to passivate defects, ZnP NP films are exposed to UV light. The passivation effect on ZnO NP films by this UV ozone treatment was investigated by photoluminescence measurements. Upon this treatment, we found that the defect band emission at 519 nm was also significantly reduced, indicating a significant reduction of defect states. As a result, due to the reduction of the defect states emission, the band-to-band emission peaked at 372 nm peak increases in intensity. It should be also noted that the UVO treatment does not only treat the ZnO films surface, it also passivates the defects in the bulk due to the porosity of the ZnO NPs films, as the PL signal is coming from both bulk rather than just the surface. The passivation mechanism here is believed to be correlated with the reduction of oxygen vacancies by the penetration of oxygen in the NPs films. As a result of this passivation, the carrier lifetime is enhanced and the recombination rate is reduced. This reduction of defects has also resulted in an enhancement in photocurrent and power conversion efficiency in polymer solar cells. The defect passivation also led to enhancement in sub-bandgap emission in organic light emitting diodes.

Guided Assembly of Anisotropic Micro-Structures Into Mesoscale Hierarchies

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Funding:	$250,000

PROGRAM SCOPE

In this project, we focus on the synthesis and fabrication of new inorganic, polymeric, and hybrid anisotropically-shaped microcrystals, microcapsules, and nanocrystals, and understanding their assembling behavior at interfaces. As a result, we expect to form hierarchical mesoscale assemblies with the plasmonic fields of the nanoparticles greatly altering the optical and physical properties. This goal is motivated by the fact that despite the wide range of inorganic nano- and microstructures, the guided formation of organized macroscopic and mesoscale materials from anisotropic building blocks has been rarely demonstrated.

FY 2012 HIGHLIGHTS

Firstly, the anisotropically shaped, micro- and nanocontainers with nanoscale shells and functionalized microparticles are fabricated by an LbL approach. The original spherical, cubic, and tetrahedral micro- and nanoparticles from different inorganic materials are modified by wrapping them with polymeric shells with different composition. The mechanical stability of the flexible spherical, cubic, and tetrahedral microcontainers had been evaluated under osmotic pressure and with computer simulation that mimicked practical situations under assembling conditions. The elastic properties and permeability of microcontainers at different pH conditions had been evaluated. Secondly, the plasmonic-active nanoparticles are assembled into two-dimensional structures and the conjugated polymers are introduced. Anisotropic plasmonic nanostructures such as gold and silver nanocubes are coupled with the conjugated polymer shells, and resulting highly variable optical properties are related to energy transfer in the core-shell structures. The observed change in the fluorescence intensity of the conjugated polymer with increasing its separation from the plasmonic surface is proposed to result from the interplay between a short-range quenching mechanism and a relatively longer range plasmonic fluorescence enhancement mechanism. Discrete dipole approximation calculation suggests that the fluorescence enhancement with silver nanocubes is caused by the plasmonic enhancement at certain distances.

Dielectric Ceramics in Nanosheet Form

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PROGRAM SCOPE

Nanosheets are characterized as being 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 is the fact that nanosheets can combine remarkable, quantum effect-derived properties with large surface areas and the advantages of solution-based manipulation methods.

We are interested specifically in metal oxide ceramics, including metal titanates $MTiO_3$ and ruthenates $MRuO_3$. The important initial challenge is that there is no bulk precursor that can simply be exfoliated to provide freestanding nanosheets of these materials. However, when this preparative hurdle is surmounted, the scientific rewards will be substantial. At a fundamental level, 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 new area of two-dimensional ceramic nanomaterials encompasses synthesis, characterization, and deposition methods. Our objectives are to (1) develop innovative methodologies for preparing dielectric ceramics in nanosheet form, (2) characterize the fundamental properties of dielectric ceramic nanosheets, and (3) process dielectric ceramic nanosheets via solution-based techniques.

FY 2012 HIGHLIGHTS

Objective (1): We have examined a range of synthetic options and found reaction conditions that allow us to transform TiO_2(B) nanosheets into $MTiO_3$ nanosheets, for M = Ba, Sr, Pb. Our characterization of $BaTiO_3$ nanosheets shows that they have the distinct, very anisotropic nanosheet morphology: thickness of 1-2 nm and lateral dimensions of several microns (SEM, TEM, AFM).

Objective (2): In-depth structural characterization (variable temperature synchrotron diffraction and variable temperature Raman spectroscopy) indicates that the crystal structure of $BaTiO_3$ nanosheets is tetragonal at room temperature and below. This fact is important as a prerequisite for ferroelectric properties as well as an interesting contrast to most $BaTiO_3$ nanoparticles that exhibit the cubic structure already at room temperature. Preliminary results with piezoresponse force microscopy (collaborator: Prof. Matt Dawber, SUNY Stony Brook Physics) provide the initial evidence that sub-2 nm freestanding $BaTiO_3$ nanosheets can indeed support ferroelectric properties.

Controlling Magnetic and Ferroelectric Order through Geometry: Synthesis, Ab Initio Theory, and Characterization of New Multi-Ferroic Fluoride Material

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Funding:	$347,958

PROGRAM SCOPE

Mixed-metal fluoride materials represent a vast and varied class of compounds. The major objective of this proposal is to develop the chemical and physical insight necessary to rationally design new multi-functional multi-ferroic fluoride materials. These materials represent a promising class of electronic, magnetic, and/or optical compounds that respond in a technologically useful way to several external stimuli. Multi-ferroic materials possess more than one 'ferro' property such as ferroelectricity, ferroelasticity, and ferro-, anti-ferro-, or ferrimagnetism. Specifically we propose to investigate new magnetically ordered geometric ferroelectric complex fluoride materials. Our approach involves a two-fold strategy: bulk synthesis, crystal growth, and subsequent characterization (Halasyamani) of new mixed-metal fluorides, and first-principles theoretical studies (Fennie) of their structural, dielectric, and magnetic properties. Ultimately our goal is to develop new microscopic models that lead to the desired macroscopic properties in this family of magnetic-ferroelectric fluorides, as well as the routes to synthesize such materials.

FY 2012 HIGHLIGHTS

Complex fluorides are an interesting class of materials to explore for new ferroelectrics and multiferroics. The elucidation of design rules for new ferroelectric fluorides is challenging because polar fluorides tend to form in structures with a large number of atoms in the unit cell and the ferroelectricity is almost always of the geometric type. In the last year, we have been developing new ideas and models to rationally design new polar fluorides from first principles. We have revealed the origin of ferroelectricity in $CsPbF_3$, the only known polar ABF_3 compound. We have found that the interplay between lone-pair localization and rotations stabilizes the rotation pattern most compatible with ferroelectricity, i.e., a-a-a-, rather than the more common a-a-c+ in which most ABF_3 compounds form. Using this compound as a guide, we have been systematically exploring other, as yet unsynthesized, $APbF_3$ compounds. Additionally we replace Pb^{2+} with another lone pair cation, Sn^{2+}. Within a perovskite manifold of states, $CsSnF_3$ is ferroelectric; yet synthesis of this compound by our experimental collaborators shows that not only is it not ferroelectric, it isn't even a perovskite. Why?

Enhanced Mixed Electronic-Ionic Conductors through Cation Ordering

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Funding: $400,000

PROGRAM SCOPE

The performance of many energy conversion and storage devices depend on the properties of mixed ionic-electronic conducting (miec) materials. Mixed or ambipolar conductors simultaneously transport ions and electrons and provide the critical interface between chemical and electrical energy in devices such as fuel cells, ion transport membranes, and batteries. Enhancements in storage capacity, reversibility, power density, and device lifetime all require new materials and a better understanding of the fundamentals of ambipolar conductivity and surface reactivity.

The high temperature properties of the ordered perovksites $AA'B_2O_{5+x}$, where A = rare earth ion, Y and B = Ba, Sr are being studied. The work is motivated by the recent discovery that members of this class of materials have some of the best oxygen transport and surface exchange rates for mixed ionic and electronic conductors. The objectives of the work are to (1) learn how to control A-site cation ordering in $AA'B_2O_{5+x}$ perovskites; (2) understand how the cation and associated anion order lead to exceptional ionic and electronic transport properties and surface reactivity, and use this understanding to develop optimized A-site cation ordered perovskites for use in electrochemical devices; and (3) understand the effects of nanostructure and strain on structure and properties

A combined experimental and computational approach, including structural, electrochemical, and transport characterization and modeling, is used. The approach attacks the problem simultaneously at global (e.g., neutron diffraction), local (e.g., nuclear magnetic resonance), and molecular (ab initio thermokinetic modeling) length scales.

FY 2012 HIGHLIGHTS

We have measured the oxygen non-stoichiometry of $PrBaCo_2O_{5+x}$ and $NdBaCo_2O_{5+x}$ by Coulometric titration. The data for both systems are characterized by a large hysteresis effect indicative of a first order phase transformation. In the intermediate regions, the kinetics are extremely slow (days). The most likely explanation for this behavior is the presence of a two-phase region between $LnBaCo_2O_{5+x}$ and a new ordered structure, $LnBaCo_2O_{5.25}$. On the same systems, we have determined the structure and oxygen non-stoichiometry as a function of temperature and oxygen partial pressure by neutron diffraction. Various structure models have been tested and used to determine the variations of the atom positions, the oxygen non stoichiometry, and the lattice parameters. All atoms were refined with anisotropic thermal parameters. The thermal motion is indicative of the oxygen ion diffusion pathway.

We have used ab initio methods to find descriptors that can predict SOFC cathode performance. We have shown area-specific resistance (ASR) and oxygen exchange rates (k*) to be correlated with ab initio calculated oxygen p-band centers and oxygen vacancy energies in mixed electronic-ionic conducting perovskites. These results represent the first time it has been shown that ab initio methods can directly predict SOFC cathode performance and the first identification of a fundamental materials property descriptor for SOFC cathodes.

Cathode Catalysis in Hydrogen/Oxygen Fuel Cells: Mechanism, New Materials, and Characterization

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Funding:	$350,000

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. We focus on new, Cu-containing catalysts for the ORR which mimic the highly efficient three-Cu center found in multicopper oxidases such as laccase. We also focus on advanced characterization of the ORR, particularly in situ x-ray methods, in order to determine physical and electronic structure changes occurring at the surface of active materials such as Pt upon oxygen exposure and reduction.

FY 2012 HIGHLIGHTS

The focus on coordination of Cu with ligands containing N to form competent ORR catalysts possibly mimicking laccase has led to an examination of several different N-containing ligands. We recently examined tris(2-pyridylmethyl)amine (TPA) and showed that this ligand, complexed with Cu, yields the most positive potential onset for the ORR in aqueous acidic solution relative to any Cu-containing complex thus far examined. Derivatives of TPA exhibit even higher onset potentials at the cost of some stability.

We monitored Pt electrocatalyst evolution during ORR electrocatalysis through use of an in-situ electrochemical x-ray absorption spectroscopy (XAS) cell developed previously. Our cell’s novel poly(dimethyl siloxane) window provides high oxygen permeation to the working electrode, permitting here-to-fore unobserved monitoring of electrocatalyst evolution during ORR electrocatalysis. Using this cell, we have produced the first comparison of Pt XAS data under N_2 sparged environment and during ORR electrocatysis.

Programming Function via Soft Materials

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Funding:	$1,607,409

PROGRAM SCOPE

The overarching goal of the proposed research effort is to establish the fundamental knowledge required to transform diverse classes of information- and function-encoded building blocks into multiscale functional assemblies that guide photon-electron conversion processes for light capture and utilization. Only by controlling the spatial organization and dynamics of materials over multiple length scales through scalable, economically viable pathways can their full potential be realized. Development of this science base will enable the assembly of new solar microcell arrays, conducting networks, and inorganic light emitting diodes in unusual mechanical and geometric layouts. Our cluster's vision for Programming Function via Soft Materials integrates three core areas: (1) dynamic supracolloidal assemblies, (2) deterministic assembly of fluid and solid inks, and (3) functional architectures for light capture and utilization.

FY 2012 HIGHLIGHTS

Our cluster reported new discoveries in the design and assembly of chemically and shape anisotropic building blocks, including both Janus dicolloids and rods. We have also developed fluid and solid inks with higher levels of functionality than previously reported, while retaining forms favorable for deterministic assembly by direct writing and transfer printing. Finally, harnessing our unique assembly capabilities, we have created flexible, highly transparent solar cell arrays; flexible inorganic LED arrays; and flexible PZT arrays in unusual layouts.

RECOVERY ACT - Templating of Liquid Crystal Microstructures by Reversible Addition-Fragmentation Chain Transfer Polymerization

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Sr. Investigator(s):	
Students:	0 Postdoctoral Fellow(s), 2 Graduate(s), 3 Undergraduate(s)
Funding:	$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

The goal of the research is to develop the fundamental knowledge necessary for the design and synthesis of chemically and mechanically robust, internally-structured polymer nanoparticles. In particular, nanoparticles with bicontinuous porous structures are desired because of their high interfacial area, their ability to encapsulate both hydrophilic and hydrophobic components, and the possibility to functionalize the particle surface makes them ideally suited for many applications. The three primary objectives of this research are designed to systematically study the ability to both tune and template the microstructures of dispersed liquid crystals using reversible addition-fragmentation chain transfer (RAFT) polymerization.

The first objective seeks to decouple the interfacial curvature of the hydrophilic/hydrophobic block copolymer interface from the solution conditions by branching the copolymer. This branching strategy is anticipated to increase the concentration range over which bicontinuous microstructures form. The second objective aims to identify critical parameters for controlling the polymerization of emulsified inverse microemulsions. RAFT polymerizations of emulsified inverse microemulsions will be studied with both traditional hydrophobic chain transfer agents and surface-active chain transfer agents to investigate the impact of chain transfer agent location on polymerization kinetics and final polymer properties. The third objective seeks to unify the fundamental knowledge provided by the first and second objectives to meet the overall goal of synthesizing internally-structured polymer nanoparticles. Liquid crystal microstructures comprised of low molecular weight, branched amphiphilic block copolymers will be dispersed in aqueous solutions and polymerized using RAFT. The effect of the location of the chain transfer agent on the polymerization kinetics, polymer molecular weight and polydispersity, and particle size, internal structure, and stability will be studied.

FY 2012 HIGHLIGHTS

Copolymer block architecture has been shown to affect the thermodynamically-favorable self-assembled microstructure in bulk, and in solution with selective solvent. RAFT polymerizations of emulsified inverse microemulsions have demonstrated transport limitations to achieving complete monomer conversion to polymer, which indicates the desired thermodynamic stability of the internal drop structure. The kinetic stability of dispersed bicontinuous microstructures is being investigated, and in the next period of research, RAFT polymerizations of these dispersions will be investigated.

Charging and Polarization of Organic Semiconductors in Energy-Efficient Circuits and Energy Capture Models: Synthesis, Electronics, and Spectroscopy

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Funding: $274,977

PROGRAM SCOPE

The main goal of this project is to develop tunable organic materials and multilayers in which interfacial voltages can be set, and where those voltages control the switching and photoresponse of devices containing such organic materials. The synthesis effort is devoted to new electron-transporting conjugated polymers and side-chain-functionalizable electron- and hole-transporting polymers. Such polymers include special stabilization against effects of ambient humidity and subunits that have the potential for dense solid state packing. We also consider elemental tellurium as a high-mobility inorganic alternative to the organics. The characterization effort is aimed at determining the energy efficiency with which polarizing charge can be embedded in films of these materials and at interfaces between them, and the stability of that charge. Thermally stimulated discharge current and scanning Kelvin Probe microscopy are key techniques used, and have provided the first characterizations of organic transistor buried interfaces while transistors are in operation. The device effort has included production of field effect transistors with tunable threshold voltage (V_t), and inverters made from those transistors showing tunable switching voltages. We have also measured polarization at heterojunction interfaces associated with hybrid transistors, photodetectors, organic solar cells, and composite thermoelectrics. Such polarization likely governs the transduction efficiency of these devices, a factor not fully appreciated in previous work. A second generation synthesis effort will include charge-stabilizing modifications to dielectric polymers and contributions of self-assembly to the charging phenomena. More complex device work will include integration of our logic devices with energy-generating components such as solar cell modules.

FY 2012 HIGHLIGHTS

We demonstrated that V_t control can be used to tune the gain and switching voltage of complementary organic inverters. We are applying these inverters to monitor and correct faults in photovoltaic or light-emitting diodes. We then studied the relationship between independently measured static potentials in the dielectrics and V_t in lateral OFETs. We found the first connection between measured OSC-dielectric interfacial potential difference and V_t shifts, and established that static charging reverses the interfacial potential built up by bias stress when operating an OFET. This bias stress neutralization was even more effective when a postive charge-stabilizing additive was incorporated in the dielectric. Separately, we also showed that interfacial potential dfferences between Te used as a semiconductor layer and adjacent organic layers determine the voltage at which field effect can be harnessed.

In work more related to diodes and photodiodes, we synthesized a series of conjugated polymers for electron-injection layers and demonstrated their activity as hosts for small-molecule electron transporters. We also used lateral diodes to show that PCBM and other molecular electron acceptors have different mechanisms of polarization at their interfaces with organic electron donors, important for understanding the activity of organic heterojunctions.

Biaxiality in Thermotropic Bent-Core and Tetrapodic Nematic Liquid Crystals

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Funding: $350,000

PROGRAM SCOPE

The goal of this project is to understand the phenomena of biaxiality in thermotropic small molecule systems. Theoretical considerations suggest several pathways to obtain the biaxial nematic phase, including mixing rod- and disk-like molecules and designing molecules having intrinsic biaxial symmetry. The project focuses on the second approach and specifically on molecules having a rigid bent-core. Among the objectives of the project is the design, synthesis, and characterization of the incipient mesophases in selected homologous series of bent-core compounds. Quantitative and definitive studies are performed using techniques such as optical retardation, synchrotron x-ray diffraction, micro-Raman, dynamic light scattering, and measurements of the components of dielectric tensor, etc. to understand their symmetry, structure, physical properties and their temperature dependence, and dynamics. Determination of phase diagrams, static and dynamic topological defect structures, and the critical behavior at various transitions are conducted to test the predictions of various theoretical models.

FY 2012 HIGHLIGHTS

Several series of new bent-core compounds that are likely to exhibit the biaxial nematic phase were synthesized. We discovered (1) a compound having a wide range (> 70 °C) nematic phase with no underlying smectic phase; (2) another compound with the nematic phase followed by the smectic-A phase [In these materials, the absence of the smectic-C phase rules out the possibilities of the biaxial character arising from smectic-C order fluctuations (also known as cybotactic groups). Conoscopic results and presence of two-brush disclinations in these cases indicate biaxiality.]; (3) the addition of chiral center to one of the terminal chains of one compound resulted in the very first chiral nematic phase in bent-core materials; and (4) the addition of a calamitic mesogenic moiety to one side of the bent-core of yet another mesogen led to the formation of a biaxial smectic-A phase below the nematic phase. These compounds are prime candidates for exhibiting the biaxial nematic phase and have been identified for further exhaustive investigations.

The three components of the dielectric tensor in previously reported bent-core systems have different values and thermal dependence, thereby providing strong evidence for the biaxial nematic phase. Micro-Raman measurements of the various uniaxial and biaxial order parameters were made in one case. In addition, we have made major progress in deciphering the sub-molecular organization in the de Vries smectic-A and the biaxial smectic-C phases, which have remained poorly understood. The nematic and smectic-C order parameters and the corresponding critical exponents were measured in the two phases. In coming periods, research will be expanded to the biaxial smectic-A and smectic-C phases in several new systems.

Electronic and Ionic Conductors from Ordered Microporous Materials

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Funding: $150,000

PROGRAM SCOPE

This project aims to develop rational pathways towards the synthesis of ordered microporous materials with tunable electron and ion transport properties. In particular, we will focus on developing new synthetic routes towards the isolation of electronically active, highly porous metal-organic frameworks (MOFs). Research will be inspired by theories and experiments tested on non-porous molecular conductors. Thus, we will undertake two conceptually different yet convergent approaches: one will take advantage of π-stacking interactions between electroactive building blocks, and another will engineer through-bond electron transfer pathways. The challenge in the former will be to maintain the relatively weak π-stacking motifs in MOFs, whose structures are dictated by stronger coordinative bonds. In the through-bond electron transport approach, the challenge will be to find parent MOF structures that are amenable to synthetic transformations that will allow redox-matching formalisms akin to organic conducting polymers (e.g., the introduction of S atoms in typical oxo-based frameworks). Finally, topochemical ion metathesis reactions are proposed for the synthesis of MOF-based Li^+ and Na^+ ion conductors. The search for new electronically active microporous materials proposed in this research is motivated by the potential impact of high surface area electron and ion conductors in thermoelectrics, electrical energy storage, electrocatalysis, and potential-swing separations, among others.

FY 2012 HIGHLIGHTS

We have demonstrated that π-stacking interactions that are typical of tetrathiafulvalene (TTF) charge-transfer salts, which are conductive at room temperature, can be maintained when a TTF derivative is used as MOF building block. Significantly, our TTF-tetrabenzoate-based material was the first example of a porous MOF with high charge mobility. The intrinsic charge mobility reported by us during this term exceeded the bulk mobility values found in commercial organic conducting polymers. We also showed that topochemical ion metathesis can be employed to access redox-active MOFs from previously redox-inactive parent structures. In the near future, we look to provide the first examples of conductive MOFs based on through-bond electron transport to extend our studies of π-stacking in MOFs by interrogating the influence of doping, pore size, and monomer identity on charge mobility and conductivity, and to generalize the ion metathesis approach as a new, rational, and facile synthetic approach to new materials in this class.

Crystallization-Driven Assembly of Conjugated-Polymer-Based Nanostructures

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Funding: $150,000

PROGRAM SCOPE

The goal of this project is to harness solution-state crystallization of conjugated polymers to construct well-defined nanoscale building blocks that will facilitate fabrication of optoelectronic devices, especially photovoltaic cells, in scalable and cost-effective ways. We seek to ultimately control the organization and, therefore, the electronic properties of matter on length-scales spanning (1) the molecular, to achieve highly crystalline semiconducting polymer-based materials capable of efficient charge transport; (2) the nanoscale, to position electron donating and accepting 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.

FY 2012 HIGHLIGHTS

In collaboration with Emrick at UMass, we have developed an approach to self-assemble hybrid organic/inorganic donor/acceptor semiconducting nanowires through solution-state crystallization of conjugated polymers. We rely on the well-known assembly of poly(3-hexyl thiophene) (P3HT) into nanowire or fibril structures induced by a reduction in solvent quality. The use of polymers end-capped with ligand functionalities (either thiol or phosphonic acid) affords fibrils whose edges are highly decorated with these groups due to the tendency of chain ends to be excluded from the crystal. We have shown that these functional nanowires are highly active to adsorption of CdSe nanoparticles or nanorods, which in turn serve to bundle fibrils together into assemblies consisting of alternating nano-scale domains of polymer and inorganic particles. Photoluminescence measurements indicate nearly complete quenching of CdSe fluorescence in these hybrid materials.

In a related effort, we have studied the formation of crystals of perylene tetracarboxy diimides (PDI) upon casting from mixed solutions with P3HT. Remarkably, the two materials each influence the crystallization behavior of each other in a process we call *coupled crystal modification*. Specifically, P3HT kinetically hinders formation of PDI crystals and passivates their lateral growth, while PDI serves as an efficient heterogeneous nucleating agent for growth of P3HT crystals. The result of this coupled crystallization is ‘shish-kebab’ nanostructures consisting of narrow (~ 10 – 100 nm) PDI wires densely coated by P3HT fibrils. We anticipate this method to tune nanocrystal morphology in donor/acceptor mixtures will yield valuable insights into the effects of morphology on photophysical behavior, and perhaps ultimately to improvements in device performance.

Interfacial Behavior of Polymers: Using Interfaces to Manipulate Polymers

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Funding:	$335,000

PROGRAM SCOPE

The interactions of polymers, block copolymers, and nanoparticles at interfaces control their assemblies in thin films. Manipulating these interactions or overcoming these interactions opens pathways to generate functional materials. Solvent annealing processes, where interfacial interactions are mediated, represent one route to achieve this control and to impart mobility to polymeric materials. The mechanism by which the directed self-assembly of the copolymer microdomains order into highly ordered and oriented arrays of microdomains with long-range lateral order is ill-understood and being investigated. Strategies have been developed to remove the minor component, so as to generate templates and scaffolds for the fabrication of nanoscopic elements for potential device applications.

Related to these goals is the influence of confinement on the morphology of block copolymers. When the natural period of the block copolymer is not commensurate with the dimensions of the confining geometry, whether this is in a thin film or a cylindrical geometry, the copolymer must respond by altering its fundamental morphology. As the dimension of the confining volume becomes comparable to the dimension of the polymer chain, the dynamics of the polymer, including the entanglement density and chain mobility, can be perturbed. Using neutron scattering to determine the chain dimensions of the confined polymer, along with the rheological characteristics, like viscosity, will be used to understand the influence of confinement on chain dynamics.

FY 2012 HIGHLIGHTS

Unidirectionally Aligned Line Patterns Driven by Entropic Effects on Faceted Surfaces: A simple, versatile approach to the directed self-assembly of block copolymers into a macroscopic array of unidirectionally aligned cylindrical microdomains on reconstructed faceted single crystal surfaces or on flexible, inexpensive polymeric replicas was discovered. A single-grained line patterns over arbitrarily large surface areas without the use of top-down techniques is demonstrated, which has an order parameter typically in excess of 0.97 and a slope error of 1.1 deg. The exceptional alignment arises from entropic penalties of chain packing in the facets coupled with the bending modulus of the cylindrical microdomains. The atomic crystalline ordering of the substrate is transferred, over multiple length scales, to the block copolymer microdomains, opening avenues to large-scale roll-to-roll-type and nanoimprint processing of perfectly patterned surfaces and as templates for magnetic storage media, polarizing devices, and nanowire arrays.

Fabrication of Silicon Oxide Nano-dots with an Areal Density beyond 1 Teradots Inch^{-2}: We applied the solvent annealing method to the PS-b-PEO and used a solvent-induced surface reconstruction, followed by a tone reversal process, to transfer the pattern from organic nano-pores to inorganic nano-dots. Solvent annealing oriented and laterally ordered the cylindrical BCP microdomains normal to the film surface over a square inch area with exceptional lateral ordering.

Symmetry Breaking for the Synthesis of Nanostructured Porous Materials

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Funding:	$244,186

PROGRAM SCOPE

The overarching theme of the program is to develop, understand, and deploy new methods for sorbent synthesis. Coordination polymers offer tremendous promise for such applications and greatly complement established materials such as zeolites and carbons. The specific goals of this project can be broadly defined as those involving reduced symmetry linker design for producing coordination polymers and coordination polymers involving mixed linkers (coordination copolymers). Relaxing the constraint of having all coordinating groups of a linker symmetry equivalent opens a dizzying array of possible new connectivities. In particular, we are focusing on tricarboxylate ligands with less than three-fold symmetry and tetracarboxylate ligands with less than four-fold symmetry. In addition, we are attempting to uncover the principles needed, and reduce them to practice, in order to create isostructural materials with expanded dimensions. With respect to coordination copolymerization, we have focused on materials arising from two or more linkers with identical coordinating functionality. We have demonstrated already that diverse structures with novel features including pore dimensions and topologies can be accessed using even simple feedstocks with this approach. We now illustrate that there is even richer potential from this approach in terms of exploiting defects as sites for post-synthetic modification and using a broader range of linkers than previously explored. The long-term impact of this work will be the development of new and less costly high performance sorbents for use in a variety of established (separations, purification) and emerging (hydrogen storage, carbon capture) technologies.

FY 2012 HIGHLIGHTS

A persistent limitation has been that achieving the highest performance is only possible with materials arising from exotic components, and therefore, such coordination polymers continue to be prohibitively expensive materials. Recently, we have been able to circumvent this limitation and use inexpensive simple molecules to build ultrahigh surface area (> 4000 m^2/g) materials. This is exemplified by UMCM-8 and UMCM-9. Both of these materials are coordination copolymers derived from two linear linkers of different lengths yielding the same underlying net. During this period, we have also advanced the use of flowing supercritical CO_2 as a superior method for complete activation of coordination polymers compared to other methods.

Computation-Guided Synthetic Strategies for Nanocomposite Electrode Structures Designed to Probe Critical Size Effects on Charge Storage and Transport

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Students:	0 Postdoctoral Fellow(s), 3 Graduate(s), 0 Undergraduate(s)
Funding:	$350,000

PROGRAM SCOPE

Through this program, templating methods will be developed for synthesizing nanostructured composite electrodes, in which a redox active phase with limited intrinsic charge carrier conductivity but high theoretical charge storage capacity is intimately interpenetrated throughout a porous host as a secondary conductive phase. The secondary phase greatly enhances electrical conductivity, maintains electrolyte access, and provides structural, functional, and mechanical stabilization. The bicontinuous structure of conductive and active phases ensures that nm-sized dimensions are precisely controlled to keep diffusion paths short and to maximize the interface between all phases. Such constructs provide new opportunities for employing charge storage materials with desirable properties (e.g., high specific capacities, specific target potentials, low cost, safety, etc.) but which were previously not considered to be usable due to low electronic conductivities, slow ion diffusion kinetics, large volume changes during charge storage and release, and/or poor reversibility. Starting model compositions of active phases include Li intercalates of lithium-transition metal silicates and oxides. The choice of materials and material dimensions will be guided by theory and computational modeling involving density functional theory. One goal will be to determine the influence of materials dimensions at the nanometer to submicrometer scales on the ability of the nanocomposites to intercalate, propagate, and/or store charges, including ions and electrons. Because of the small dimensions and large interfaces of the nanostructured composites, charge storage may involve both redox mechanisms and surface or space charges. The fundamental information on the influence of size and interfacial effects of electroactive materials to be gained from this research is relevant for the design of new anode and cathode materials for rechargeable batteries and for hybrid charge storage devices that combine redox storage mechanisms with capacitive storage.

FY 2012 HIGHLIGHTS

During the first two months of this new project, we have begun to develop syntheses for lithium-transition metal silicate thin films and nanotubes (transition metal = vanadium, nickel) and lithium zirconium oxide bulk particles. These will be fully characterized and subsequently incorporated in nanocomposites with carbon to investigate lithium intercalation/deintercalation properties. On the computational side, we have validated that the CM-5 charge model can reliably describe charge distributions in solids and that it can be applied to lithium zirconium oxide systems. We have tested the change in charge distributions upon removal of Li atoms and Li^+ ions from small clusters.

Pan American Advanced Studies Institute Program (PASI)

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Funding:	$200,000

PROGRAM SCOPE

Pan-American Advanced Studies Institutes are short courses of ten days to four weeks' duration, involving lecturers of international standing at the advanced graduate and postgraduate level. PASIs aim to support interdisciplinary research to disseminate advanced scientific and engineering knowledge and stimulate training and cooperation among researchers of the Americas in the mathematical, physical, and biological sciences; in the geosciences and the computer and information sciences; and also in engineering fields. Proposals in other areas funded by NSF may be considered on an ad hoc basis subject to consultation by the PI with the PASI program prior to proposal submission.

The typical PASI format is for a group of 10 to 15 renowned researchers to offer lectures for the benefit of 40 to 60 advanced graduate students, professional engineers, or recent post doctorates from several countries in the Americas, at least half of which must be from the United States. The institutes can be sited in any part of the Hemisphere. Many have attracted support from local and other national agencies and organizations.

The program is jointly supported by the Directorate for Biological Sciences, the Directorate for Mathematical Sciences and Physical Sciences, the Directorate for Engineering, the Directorate for Geosciences, and the Directorate for Computer and Information Science and Engineering—hereafter referred as the participating directorates—as well as the Office of International Science and Engineering (OISE) at NSF, and the Office of Basic Science of the Department of Energy. OISE will manage all pre-award and post-award actions. The program announcement appears as Program Solicitation NSF 12-535 at the NSF web site.

FY 2012 HIGHLIGHTS

PASIs funded in the FY2012 competition:

“Pan-American Advanced Studies Institute (PASI) on Polymer and Composite Materials from Renewable Resources and Biorefinery from Chemistry to Applications.” Organizer: Dr. Maria l. Auad, Auburn University. OISE-1242213

“Pan-American Advanced Studies Institute (PASI) on the Science of Predicting and Understanding Tsunamis, Storm Surges, and Tidal Phenomena.” Organizer: Dr. Lorena Barba, Boston University. OISE-1242245

http://www.bu.edu/pasi-tsunami

“Pan-American Advanced Studies Institute (PASI) on Atmospheric Processes in Latin America and the Caribbean: Observations, Analysis, and Impacts.” Organizer: Dr. John Braun, University Corporation for Atmospheric Research. OISE-1242281

Research Facilities at ChemMatCARS: A Synchrotron Resource for Chemistry and Materials Science at the Advanced Photon Source

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Funding:	$240,000

PROGRAM SCOPE

The Division of Chemistry and the Division of Materials Research at the National Science Foundation, and the Office of Basic Energy Sciences at the Department of Energy provide continuing support to ChemMatCARS at the Argonne Advanced Photon Source under the Chemistry Research Instrumentation and Facilities Program. The award provides maintenance, operation, and selected upgrades of this unique resource as a national user facility for the chemical and materials science communities. The major techniques supported by the facility include chemical crystallography, surface science, small-angle x-ray scattering, and wide-angle x-ray scattering. The instrumentation can be adapted to accept a wide variety of user chambers for specialized sample environments.

FY 2012 HIGHLIGHTS

In FY 2012, the facility took advantage of the benefits of the upgrade of the x-ray beam delivery which terminated in late 2011. For the energy range of 6-32 keV, the new optics resulted in a beam with increased brilliance (x-ray flux) on sample and a more homogenous wave front. In addition, beam stability significantly improved. This enabled an enhancement of the user throughput as well as new experiments in photon correlation spectroscopy imaging and scattering from nanoparticle systems and interfaces. Some notable user results include work on characterization of nanoparticles used in consumer sunscreen for the purposes of understanding the safety issues related to their use; in situ dissolution–recrystallization processes, which are major concerns for all rechargeable batteries; experiments on tuning ion correlations at an electrified soft interface; water-interface properties of poly (ethylene oxide) brushes; and precise bonding information in photoactive compounds, and supramolecular and complex magnetic systems.

The upgrade also resulted in an extension of the x-ray range to 70 keV, and initial feasibility experiments with selected user groups were successfully performed. This expanded range will enable experiments not accessible at the lower x-ray range in areas of real time processing, heavy element systems, buried interfaces, and precise charge density determinations. User experiments included scattering of high-energy (60 keV) x-rays to study in-plane structures from liquid surfaces of salt solutions to understand ion coordination at surfaces, and structural and electron density determination above 40 keV. The experiments were successful and point the way to additional upgrades in infrastructure and x-ray detection that will be needed in order to take full advantage of the x-ray beam.

ChemMatCARS hosted over 400 unique users in FY 2012 and conducted 240 individual experiments at the beamline. Over 40 articles and 6 PhD theses based on work were published.

Basic Surface Chemistry and Physics of Carbon-Based Electronic Materials Modified by Silane Molecular Layers

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Funding: $133,000

PROGRAM SCOPE

The overall goal of this program is to investigate fundamental aspects of molecular self-assembly and opto-electronic properties of the important class of emergent electronic materials—small-molecule organic semiconductors. We use highly ordered molecular crystals (or highly crystalline films) as an experimental test-bed in which extrinsic defect-related phenomena are minimized or eliminated. The purpose is to understand the surface structure of these materials, their functionalization with self-assembly monolayers (SAM), and how it affects the charge transport, relevant to the operation of novel electronic devices, such as transistors, sensors, and solar cells. The long-term impact of this project will be our better understanding of the intrinsic structure-property relationship for organic semiconductors in their pure form and with SAMs, as well as an understanding of the fundamental charge transport mechanisms in organic electronics.

FY 2012 HIGHLIGHTS

We have investigated two major aspects of charge transport in organic field-effect transistors (OFETs): (1) effect of trapping on operational stability of OFETs and (2) electro-mechanical stability (flexibility) of solution-processed OFETs fabricated on ultra-flexible polymer substrates.

In the first study, we observed that in many materials, field-effect mobility—an important parameter used to characterize OFETs—strongly depends on the rate of the gate voltage sweep during the OFET measurement. Some molecular systems are so dynamic that their nominal mobility can vary by more than one order of magnitude, depending on how fast the measurements are performed, making an assignment of a single mobility value to devices meaningless. It appears that dispersive transport in OFETs with disorder is responsible for such a dynamic effect. The paramount significance given to a single mobility value in the organic electronics community suggests that such an issue is in fact a very important point to consider when engaging in fundamental studies of charge carrier mobility. [Phys. Chem. Chem. Phys. 14, 14142-14151 (2012)].

In the second study, we performed an investigation of charge transport in highly crystalline solution-processed organic semiconductors as a function of mechanical strain. We used small molecules crystallized on thin plastic sheets, resulting in high-performance flexible OFETs. These devices can be bent multiple times without degradation to a radius as small as 200 µm, demonstrating that crystalline solution-processed organic semiconductors are intrinsically highly flexible. This basic study suggests that solution-processable organic semiconductors are suitable for applications in flexible electronics. [Nature Comm., DOI: 10.1038/ncomms2263, in press (2012)].

Spectroscopic Studies of Materials for Electrochemical Energy Storage

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Funding:	$180,000

PROGRAM SCOPE

This research program centers on spectroscopic investigations of materials germane to lithium metal and lithium ion batteries. The primary analytical tools used in this investigation are solid state nuclear magnetic resonance (NMR) and synchrotron x-ray absorption spectroscopy (XAS). The NMR measurements are conducted primarily at Hunter College, and the XAS is done at Brookhaven's NSLS through an existing collaborative arrangement with NIST's beamline facilities there. The materials research is highly collaborative and leverages the efforts of long-time and more recent colleagues at universities and national labs. Some of these collaborators are listed in the sections below in the context of specific projects.

FY 2012 HIGHLIGHTS

Single crystal olivines, $LiMPO_4$, where M = Co, Fe, Mn, and Ni are being investigated by ^{7}Li and ^{31}P NMR to extract the local magnetic environments about the Li and phosphate ions, knowledge of which can provide vital experimental input to colleagues engaged in first principle calculations related to ion transport properties. In collaboration with the Ames DoE Lab (having provided samples), we have successfully mapped out the magnetic susceptibility tensors in the Fe and Co analogues; and measurements of the Ni and Mn compounds are now underway. New methods of probing the composition of the Solid Electrolyte Interphase (SEI) are now under development and are being exploited in this project, including the use of ^{13}C isotopic enrichment of electrolyte solvents. Ion transport is being investigated in polymer electrolytes of two basic kinds: membranes containing ionic liquids, and solvent-free PEO-based materials in which partial chain alignment is achieved by magnetic means. We have recently demonstrated enhanced alignment in PEO Li salt complexes containing carbon nanotubes. Regarding basic characterization of transport properties in ionic liquids, our group, in collaboration with W. Henderson's group (NC State), was the first to use natural abundance ^{13}C pulsed field gradient NMR to measure self-diffusion coefficients in hydrogen and fluorine-free IL cations. Some of these methods are now being applied to investigate sodium analogues (both ionic liquids and polyethers) for possible application in Na batteries. Finally, in collaboration with NASA/JPL, we have characterized SEI formation on lithium ion MCMB anodes using solid state ^{7}Li, ^{19}F, and ^{31}P NMR in cells containing various electrolyte additives and subjected to accelerated aging.

Bimetallic Electrochemical Displacement Materials Yielding High Energy, High Power, and Improved Reversibility

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Funding:	$200,000

PROGRAM SCOPE

Bimetallic oxides ($M_xM'_yO_z$) and phosphorous oxides ($M_wM'_xP_yO_z$) are materials worthy of investigation as cathodes for secondary lithium batteries. Through appropriate material design, one metal (M^+) will be electrochemically reduced to form conductive metallic nanoparticles, while the second metal (M'^{n+}) will provide a framework that will enable reversible electron transfer.

Through targeted design, preparation, and electrochemical study of novel bimetallic electrochemical displacement materials, this project will contribute to the knowledge base that is needed to address the practical demands of energy storage systems. This project will provide the fundamental insights needed to advance the three key performance metrics for energy storage: energy density, power delivery, and reversibility.

FY 2012 HIGHLIGHTS

Significant progress was made in the development of tunable synthesis, characterization, and electrochemistry of bimetallic materials. Silver hollandite and silver ferrite are particularly notable due to their reversibility.

We demonstrated synthetic control of the silver content in silver hollandite, $Ag_xMn_8O_{16}$, where the silver content ranges from $1.0 \leq x \leq 1.8$. This level of compositional control was enabled by the development of a lower temperature reflux-based synthesis. Notably, the synthetic variance of the silver content was accompanied by a concomitant variance in crystallite size as well as surface area and particle size. We verified the retention of the hollandite structure by conducting the first Rietveld analysis of silver hollandite on samples of varying composition. The impacts of silver content, crystallite size, surface area, and particle size on electrochemical reversibility were examined under cyclic voltammetry and battery testing where the smaller crystallite size material showed enhanced electrochemical performance.

The first electrochemical study of silver ferrite ($AgFeO_2$), a member of the delafossite family of materials, was conducted where cyclic voltammetry and test cell results demonstrated electrochemically activity. This is one of the first examples of a bimetallic delafossite structured material as a cathode in a lithium-based battery, including investigation of rechargeability for secondary battery use. SEM, EDS, and XRD revealed Ag^0 metal formation upon discharge, consistent with an electrochemical reduction-displacement mechanism. Under a cycle life test at a C/5 rate, the material consistently retained its capacity from 2 to 50 discharge-charge cycles.

Fundamental Science of High Open Circuit Voltage Excitonic Solar Cells

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Funding:	$250,000

PROGRAM SCOPE

The primary focus of the program is the use of special soft x-ray characterization methods to investigate and understand organic devices with a particular focus on organic photovoltaics (OPV). Tremendous effort is presently focused on the development of high performance OPV cells since they are predicted to have numerous attractive technological characteristics, including low manufacturing cost, mechanical flexibility, and low weight. While significant progress has been made in the synthesis and processing of organic semiconductors for solar cell applications, progress has been largely by trial-and-error, and there is a pressing need for comprehensive understanding of the device structures created and their relation to the molecular structure and thermodynamic properties of the materials. Overall, we pursue a coherent strategy to address fundamental science of three critical areas of bulk heterojunction solar cells and their role in device performance: (1) domain purity/miscibility; (2) morphology (size, multiple lengthscales/hierarchies); (3) interfaces (roughness, interdiffusion, molecular ordering). These device characteristics cannot be assessed adequately with other analysis tools. We also link structural details to fundamental materials characteristics such as the fullerene miscibility in the donor polymer and to fundamental interactions with solvents mixtures used to fabricate these devices.

FY 2012 HIGHLIGHTS

We have made significant progress on two fronts.

(1) We have extended our pioneering measurement of fullerene miscibility in the amorphous portions of semi-conducting polymers that are used as donors in organic solar cells. We have observed that generally there is a difference in miscibility that depends on fullerene type (PC61BM versus PC71BM). Furthermore, and most significantly, we have shown that the miscibility is a general phenomenon that occurs for all materials presently used. We have already used this concept to show why some devices work well and how their performance depends on processing. Molecular level interactions are thus a critical device parameter that needs to be considered when designing new materials or new fabrication protocols.

(2) We have developed a novel tool that is sensitive to molecular orientation and ordering in relation to a local reference, such as the donor:acceptor interface in a solar cells. Furthermore, such ordering was shown to be critical in a number of high performance materials systems. Methods to characterize preferential orientation at bulk heterojunctions were previously lacking and, therefore, left this potentially important parameter for achieving high performance unexploited and uncontrolled.

Linking Ion Solvation and Lithium Battery Electrolyte Properties

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Funding: $240,000

PROGRAM SCOPE

The research objective of this proposal is to provide a detailed analysis of how solvent and anion structure govern the solvation state of Li^+ cations in solvent-lithium salt mixtures and how this, in turn, dictates the electrolyte physicochemical and electrochemical properties which govern (in part) battery performance. Lithium battery electrolytes remain a poorly understood and hardly studied topic relative to the research devoted to battery electrodes. This is likely due to the fact that it is the electrodes which determine the energy (capacity) of the battery. The electrolyte, however, plays a crucial role in the power, low and/or high temperature performance, lifetime, safety, cost, etc. In particular, the state-of-the-art electrolyte composition consisting of $LiPF_6$ with ethylene carbonate and a linear carbonate such as ethyl methyl carbonate has undergone only minor changes over the past two decades. This electrolyte is poorly optimized for use with new electrode materials for advanced Li-ion batteries or for batteries subjected to demanding applications (e.g., traction batteries in plug-in hybrid electric vehicles). We believe that the development of a "looking glass" into the molecular interactions in bulk electrolytes through a synergistic experimental approach involving three research thrusts will complement work by other researchers to optimize multi-solvent electrolytes and to understand and control the electrode-electrolyte interface, thereby enabling the rational design of electrolytes for a wide variety of battery chemistries and applications (low/high temperature, high power, etc.)—electrolytes on demand. These three research thrusts include (1) exploration of the ionic association behavior of select lithium salts with a wide variety of solvents, (2) conduction of an in-depth analysis of the thermal phase behavior of diverse solvent-lithium salt mixtures, and (3) determination of electrolyte physicochemical and electrochemical properties for comparison with the ionic association and phase behavior.

FY 2012 HIGHLIGHTS

The thermal phase behavior, solvate crystal structures, and solution structure for a range of mixtures consisting of nitrile, cyclic carbonate, and cyclic ester solvents have been determined with a number of lithium salts ($LiBF_4$, $LiClO_4$, $LiPF_6$ and $LiN(SO_2CF_3)_2$ (i.e., LiTFSI)). This information has then been directly correlated with transport data (viscosity, conductivity, molar conductivity) to explain the origin of variations in the properties of the electrolytes. In addition, the solvate crystal structures have been used to clarify the correct assignment of Raman anion vibrational bands for the determination of anion...Li^+ cation coordination (i.e., ionic association interactions) with $LiBF_4$, $LiClO_4$, $LiPF_6$, and LiTFSI. This work lays the foundation for the development of a Li^+ Cation Solvation Scale.

Actinide Transition-Metal Chalcogenides and Pnictides

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Funding: $70,000

PROGRAM SCOPE

The objective of this project is to increase our knowledge and understanding of Th, U, and Np solid-state chemistry. It will involve the synthesis of new compounds and their structural characterization by means of single-crystal x-ray diffraction techniques. In addition, it will involve the measurement of diverse physical properties of the compounds. These will include optical, magnetic, and transport measurements, mainly on single crystals. Theoretical insights into the results will be obtained through DFT and related calculations. Compounds of interest will contain a transition metal and an actinide (Th, U, or Np) in combination with a chalcogen (S, Se, or Te) or a pnictogen (P, As, Sb, Bi) or both. Few compounds of this type, especially those containing Np, have been synthesized and their physical properties studied.

FY 2012 HIGHLIGHTS

Our present work on U and Th compounds has led to a number of new compounds, many of which have new structure types and interesting magnetic properties. Detailed results on $Tl_3Cu_4USe_6$, $Tl_2Ag_2USe_4$, $Cs_2UPd_3Se_6$, MnU_8S_{17}, $Np(PS_4)$, $Np(P_2S_6)_2$, $K_{11}Np_7(PS_4)_{13}$, $Rb_{11}Np_7(PS_4)_{13}$, $ZrLa_2S_5$, β-UPSe, $CsU_2(PO_4)_3$, $Ba_8Hg_3U_3S_{18}$, $UYb_2O_2Se_3$, $U_2Ln_2O_4Se_3$ (*Ln* = Pr, Sm, Gd), SUO, US_2, $Cs_3U_{18}Se_{38}$, $UEr_2O_2S_3$, nine compounds in the $A_2UM_3Q_6$ family, $A_2U_6Pt_4Q_{17}$ compounds, and ThOQ have been published. Some of this work involved collaborations with David Shuh (LBNL), Lester Andrews (Virginia), and Dr. Eun Sang Choi of the National High Magnetic Field Laboratory. Planned to be completed in the next budget period are the syntheses, structures, and physical properties of Np_2Se_5, Th_2Se_5, $Rb_2Th_7Se_{15}$, $Rb_4[U_2(P_2Se_6)_{2.5}(Se_2)]$, and several new Ba/U/M/Se compounds.

Chemistry and Properties of Complex Intermetallics from Metallic Fluxes

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Funding: $150,000

PROGRAM SCOPE

This project investigates the reaction chemistry and synthesis of new intermetallic materials with complex compositions and structures using metallic fluxes as solvents. The metallic fluxes offer several key advantages in facilitating the formation and crystal growth of new materials, including liquid aluminum, gallium, and indium. The purpose of this project is to exploit the potential of metallic fluxes for materials discovery in intermetallics and open new paths to compound formation. We seek to (1) discover new Si (or Ge)-based compounds with novel structures, bonding, and physicochemical properties; (2) learn more about the reaction chemistry that is responsible for stabilizing such materials and study their structural interrelationships to ultimately be able to predict their existence; and (3) identify and characterize the complex phases present in many advanced Al-matrix alloys. Such phases play a key role in determining (either beneficially or detrimentally) the mechanical properties of Al-matrix alloys.

FY 2012 HIGHLIGHTS

We achieved the synthesis of single crystals of the unusual material $YbMn_{0.17}Si_{1.88}$ utilizing indium as metal flux. The crystal structure of $YbMn_{0.17}Si_{1.88}$ was refined using X-ray single crystal data. $YbMn_{0.17}Si_{1.88}$ crystallizes from indium flux in the polar non-centrosymmetric space group $P2_1$. The compound orders antoiferromagnetically at 4.51 K, and the magnetic properties are consistent with mixed valent or intermediate valent Yb atoms. An uncommon negative magnetization is observed in $YbMn_{0.17}Si_{1.88}$ at ~5.8 K, and this interaction is prominent at lower field, which makes the total magnetic moment of $YbMn_{0.17}Si_{1.88}$ negative. The Mn spins influence on total magnetism is evident from the field dependent magnetic susceptibility, magnetization, and specific heat studies which should further be studied with neutron diffraction and magnetic structure calculations. A hint of non-Fermi-liquid behavior is observed in the low-temperature part of Cp(T)/T. Systematic temperature and magnetic field dependent structural, thermal, transport, and magnetic measurements of $YbMn_{0.17}Si_{1.88}$ may bring out the underlying physical phenomenon.

In another highlight of this work, we discovered that Yb_4TGe_8 (T = Cr-Ni, Ag) compounds and the structural analogue Gd_4CrGe_8 feature Ge-square nets with structural distortions similar to a charge density wave (CDW) and long-range ordering of T vacancies. The planar nets of Ge atoms are cross-linked in the third direction with square pyramidal T atoms. The compounds exhibit zero thermal expansion (ZTE) in the plane of the square nets from 10-300 K and zero volume expansion below ~160 K. The three-dimensional atomic arrangement in RE_4TGe_8 enables a Poisson-like mechanism that allows the structure to contract along the direction of the Ge planes as it expands slightly in the perpendicular direction. The CDW-like modulations in the Ge nets create sequences of long/short Ge-Ge distances, which impart significant in-plane compressibility that accommodates the contraction.

Materials Science of Electrodes and Interfaces for High-Performance Organic Photovoltaics

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

PROGRAM SCOPE

The research goals of this 5-PI effort are: (1) Design (based on theory and computation), synthesis, and characterization for high-performance organic photovoltaic (OPV) cells having advanced TCO (transparent conducting oxide) electrode layers with high conductivity and transparency but without (or minimizing) the use of indium. (2) Development of a theory-based understanding of what is the best configuration for the ideal interface between oxide electrodes/interfacial layers and OPV active layers composed of current-generation molecules and polymers. (3) Exploration and development of new processing techniques and cell architecture for the next generation of large-area flexible OPVs. It is our plan that results from our research will continue to lead the way and support other DOE-funded energy programs. During the first 16 months of this highly interdisciplinary program, significant progress has been made in each of the above areas.

FY 2012 HIGHLIGHTS

In a joint collaboration, the Mason, Freeman, and Poeppelmeier groups investigated the TCO properties of the so-called “homologous series” of compounds in the In-Zn-O system, $In_2O_3(ZnO)_k$ (k = various integer values). By combined in situ high temperature “Brouwer analysis” (log-log plots of electrical properties vs. pO_2) and first principles calculation of defect formation energies, the majority defect species were identified.

Chang has developed a process to synthesize 3D TCO nanowire-arrays as electrode structures. In particular, they successfully fabricated lithographically-patterned ITO nanowire arrays with varying heights (up to 15 microns) and spacings as close as 400 nm. Using these wires, they were able to fabricate solar cells with 3D geometry. Preliminary experiments have indicated that cell efficiency can be improved by as much as 30% for the case of dye sensitized solar cells (DSSCs). This is due to improved charge collection and transport within the cell, and is now being applied to OPVs in collaboration with Marks.

Marks demonstrated that the conduction band minimum (CBM) of transparent post-transition metal amorphous oxide semiconductors can be specifically tuned for various fullerene acceptors in OPV active layers. For example, optical measurements show that continuous tuning with composition of the CBM in thin films of amorphous $In_{2-x}Ga_2O_3$ (a-IGO) is possible using combustion synthesis techniques, previously developed at Northwestern. Using these a-IGO materials as interfacial layers in inverted OPVs having a ITO/a-IGO/PTB7:PC71BM/MoO_3/Ag geometry, it is shown that performance is sensitive to the Ga content with maximum OPV performance (e.g., power conversion efficiency) achieved for Ga contents in the 60 – 70% range. Thus, the properly aligned CBMs and deep lying VBMs of post-transition metal oxide semiconductors enables durable OPV cells with power conversion efficiencies greater than 8%, and without using conventional interfacial layers.

Molecular Processes Underlying the Structure and Assembly of Thin Films and Nanoparticles at Complex Interfaces

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Funding:	$260,000

PROGRAM SCOPE

Many important new materials are being made in increasingly complex and reactive environments. The assembly of thin films at liquid/solid and liquid/liquid interfaces fall into this category as do the multitude of unique nanostructured materials that assemble in solvents and at surfaces. This increased complexity of the materials growth environment is usually accompanied by less predictability, often because of our limited knowledge of the fundamental molecular interactions that lead to the assembly and stability of materials at these interfaces. The focus of the science in this project is to obtain a molecular-level picture of adsorption and assembly at complex "soft" interfaces. The studies include (1) nanoparticle assembly at liquid surfaces and (2) charged macromolecular assembly at aqueous/hydrophobic liquid surfaces. The studies are conducted using vibrational sum frequency spectroscopy to obtain the molecular structure of interfacial species, interfacial tension and zeta potential measurements, light scattering, and molecular dynamics simulations.

FY 2012 HIGHLIGHTS

Our most recent examination of the assembly of the carboxylate containing polyelectrolyte polyacrylic acid (PAA) is the first measurement to directly probe the adsorption and orientation characteristics of a polyelectrolyte at the neat oil-water interface in the presence of mono and divalent metal ions. In our initial investigations of PAA adsorbing to the CCl_4-water interface, we found remarkable sensitivity in the adsorption process to the aqueous phase pH. The pH studies suggested that the adsorption is a multistep process that depends strongly on PAA charge density—a result that is further supported and clarified in this more recent work. We have found that this adsorption process is significantly affected by the presence of aqueous phase ions that can alter the electrostatics and conformation of the polymer, in some cases driving the polymer to the interface under conditions where adsorption otherwise was prevented. The studies show that at the critical pH (i.e., pH 4.5), Ca^{2+} and Mg^{2+} ions interact strongly with carboxylate groups both along the backbone of the polymer and through the displacement of solvating water molecules around the carboxylate groups, the net effect being enhanced adsorption of highly oriented polymer at these higher pHs. Due to the metal ions screening the anionic charge, the carboxylate functional groups are able to achieve a net orientation at the interface, pointing into the water phase. Na^+ ions, like the divalent ions, have the ability to enhance PAA adsorption but lack the capacity to screen the anionic charge, resulting in a lack of carboxylate orientation. The results have implications for understanding interfacial processes of importance in biological and environmental sciences, specifically in the case of the placement of toxins and nutrients within the environment.

Research Project on the Recruitment, Retention, and Promotion of Women in the Chemical Sciences

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Funding:	$0.00 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

Global competition and rapid advances in science and technology requires that the nation's technical workforce be comprised of the best and brightest individuals. No segment of the population can be ignored or overlooked in this search for talent, as diversity in opinions, ideas, and experiences is known to fuel creativity and innovation. This program supports COACh research around efforts to increase the diversity of the STEM workforce. COACh is a grassroots organization of U.S. women scientists and engineers that is widely recognized as one of the most successful programs of its type. Since it began in 1997 with support from DOE, it has worked with over 8,000 women and minority scientists and engineers in their quest to become successful in their research and career objectives. The objectives of the current projects are to (1) expand COACh survey research on the quality and impact of COACh activities; (2) conduct interview and survey research on the experience of underrepresented minority women in STEM fields and use the results to develop COACh programs that educate the community and provide assistance to the advancement of minority groups; (3) expand COACh research and strategic efforts to increasing the recruitment, retention, and success of women scientists and engineers in two DOE National Laboratories; and (4) conduct new research aimed at increasing the social capital of women scientists and engineers through the development of new COACh networking workshops and on-line activities, and use our research team to evaluate their effectiveness.

FY 2012 HIGHLIGHTS

Over the past two years, our researchers have been examining the elements that have contributed to the high success and impact of COACh programs. Data examined came from records kept by the group, observations of their activities, and extensive reflections of key participants. Sponsored activities included workshops to teach important career-related skills and promote networking activity and other efforts to promote change in policies and practices in the field. Concepts from the social science literature regarding successful organizations have been applied to the analysis. Important COACh elements identified are strong and consistent leadership, use of social networks to maintain a diverse and committed membership, using data to develop and change programs, and an organizational culture that supports norms promoting deliberative task orientations and a supportive socio-emotional climate. Four suggestions are provided for groups wanting to replicate its success. (1) Have a deliberative, long-term process. (2) Involve a diverse and dedicated group of people devoted to the group's culture and goals. (3) Promote a culture that attends to both socio-emotional and task-oriented norms. (4) Develop sufficient, long-term monetary and logistical support. The long-term support of the COACh program by funding agencies such as DOE has been a key element the success of this COACh.

Bi-Continuous Multi-Component Nanocrystal Superlattices for Solar Energy Conversion

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Funding:	$1,520,000

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 NC 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 and the physical phenomena that govern the flow of energy and the transfer and transport of charge important in converting solar energy into electricity.

FY 2012 HIGHLIGHTS

Wet-chemical synthetic routes were used and developed to prepare a wide-range of semiconductor and metal NC samples tunable in size from ~2-20 nm in diameter and monodisperse to ≤5%, providing many different building blocks for the self-assembly of single and multi-component NC superlattices. In particular, we developed an improved synthesis and corroborating simulations of Au nanorods, which allows the longitudinal surface plasmon resonances to be tuned from 627 nm to now 1246 nm. We organized NCs into single and multi-component superlattices into uniform NC layers by different coating and transfer methods.

Collective physical phenomena between neighboring NCs in close-packed arrays give rise to novel and fascinating electronic, optical, and optoelectronic properties. In competition with energy transfer, carrier tunneling between neighboring NCs allows for charge transport and observations of photo- and dark-conductivity. In early reports, conductivities were very small as the long, insulating aliphatic ligands used in the synthesis and assembly of the NCs gave rise to highly resistive materials requiring low-level current measurements. We recently introduced a new, compact thiocyanate ligand for nanocrystals. We realized high performance, balanced electron and hole mobilities in PbS nanocube FETs, which we exploited to demonstrate the first non-sintered quantum dot based circuits. While most studies of photoconductivity and charge transport have been pursued on small bandgap Pb-chalcogenides, we demonstrated dramatic performance enhancement in wider band gap CdSe NC thin films. By combining strong-coupling (through the use of the thiocyanate ligand) and by doping (through a process of thermal diffusion, not previously used in NC thin films), we realized band-like transport in CdSe NC thin films will carrier mobilities as high as 27 cm^2/Vs.

New Superconducting Materials

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Funding:	$186,000

PROGRAM SCOPE

The goal of this program is to find new superconducting materials and to investigate the relationships between the chemistry, structure, and properties of known superconductors, with the goal of using those relationships to find new superconducting materials. A new superconducting material that can carry a significant amount of current at a sufficiently high temperature would have a profound impact on our nation's energy infrastructure when used in power transmission lines, and thus success in this project could have wide-ranging implications. Our current work concentrates primarily in the area of superconductivity in the compounds of transition elements with phosphorus and germanium. We have found a new kind of structure-property relationship in superconducting phases in this chemical family, specifically between the magnetic and electronic properties and the presence of a molecule-like bond in compounds with the very common $ThCr_2Si_2$ structure type. These compounds are the basis for the high temperature iron arsenide superconductors that are of so much recent interest and for many other superconductors as well. Work of theoretical chemist Roald Hoffman on this crystal structure type (the AT_2X_2 structure) in the 1980s argued for the critical importance of the shape of the TX_4 tetrahedra and X-X molecular dimer-like bonding across the A layers in determining the electronic states at the Fermi level. Establishing the critical nature of this X-X molecular dimer has been one of the major thrusts of our work. Another approach for finding new superconductors that we are pursuing concentrates on materials based on transition metal dichalcogenides. For these materials, there is a competition between superconductivity and the formation of charge density waves—a different kind of collective state of the electrons. We are working to find ways to make charge density waves electronically unstable so that superconductivity will "win" the competition and be found in a larger number of compounds.

FY 2012 HIGHLIGHTS

We completed work on the $BaNi_2(Ge_{1-x}P_x)_2$ system. The in-plane X-X (X = $Ge_{1-x}P_x$) dimer formation present in the end member non-superconducting $BaNi_2Ge_2$ compound, which results in a structural transition to orthorhombic symmetry, is completely suppressed to zero temperature on P substitution near x = 0.7. When this dimerization is suppressed by chemical doping, a dome-shape superconducting composition region with a maximum T_c of 2.9 K emerges. Clear indications of phonon softening and enhanced electron-phonon coupling are observed at the composition of the structural instability where the dimerization disappears. Our findings show that chemical dimer breaking offers new possibilities as a tuning parameter for superconductivity.

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

PROGRAM SCOPE

The synthesis of new complex uranium- and thorium-containing oxides and the investigation of their physical properties is of interest and of national importance for identifying new ceramics for long-term waste storage, developing new materials for fuel rod assemblies, and training the next generation of radiation worker. Achieving these goals will require complex uranium- and thorium-containing oxides with substantially new compositions and structures, and the involvement and training of graduate students in the synthesis process. However, the preparation and characterization of new oxide compositions is not a trivial undertaking and requires a targeted approach. We therefore propose two complementary approaches to achieve the synthesis of new complex uranium- and thorium-containing oxides based on (1) the synthesis of polycrystalline powders having compositions predicted by radius ratio rules and (2) a materials discovery approach based on crystal growth from high-temperature solutions. In the first part of this proposal, the radius ratio rule approach for predicting new compositions and structures of uranium- and thorium-containing oxides is described as well as the synthetic methodology that will yield polycrystalline powders of the target phases. In the second part of the proposal, the discovery based crystal growth from high temperature solutions is detailed.

The two proposed areas are expected to come together in a convergent fashion, as one goal of this proposed work is to prepare both polycrystalline powders and single crystals of each new material prepared. Thus, new compositions identified and prepared as polycrystalline powders will be used to pursue crystal growth in diverse reaction environments that are designed to create the specific conditions necessary for the formation of the desired crystalline products, while new compositions prepared via crystal growth will provide us with the target stoichiometry for the synthesis of polycrystalline samples. This way both crystals and powders are available for structural characterization and property measurements.

FY 2012 HIGHLIGHTS

We have successfully prepared a new family of uranium(IV) containing mixed metal oxalates and have characterized their structures and magnetic properties. We have established the conditions under which some oxides containing uranium in different oxidation states can be obtained and have isolated several new phases. We have discovered a new method for preparing new complex uranium fluorides and have begun the investigation of these materials.

Mitigating Breakdown in High Energy Density Perovskite Polymer Nanocomposite Capacitors

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Funding:	$150,000

PROGRAM SCOPE

Current electrical energy storage technologies do not meet the exacting demands of commercial, residential, and transportation applications in terms of energy density. For example, the conversion from gasoline-powered vehicles to all-electric vehicles requires higher energy density pulsed power sources. Such applications require a new generation of robust dielectric capacitors that have (1) high electrical energy density (D, where $D = 0.5\varepsilon'\varepsilon_0 E_{bd}^2$), (2) low dielectric loss, (3) high field endurance, and (4) increased temperature stability and environmental ruggedness. The most promising solution to this problem is to utilize polymer nanocomposites, whereby high permittivity inorganic nanocrystals are integrated into a robust polymer matrix. In such an approach, the polymer provides the processibility, light weight, and high breakdown voltage (E_{bd} >250 V/μm), while the inorganic filler delivers the desired dielectric characteristics (ε' >300). The fundamental challenge for these composites lies in aggregation of the inorganic filler at the percolation threshold (~15 vol%), which leads to a precipitous drop in breakdown voltage (the dominant term in electrical energy density) as the continuous particle network becomes a pathway for charge carriers. To solve this problem and maximize the energy density of the resulting nanocomposites, our specific deliverable objectives are two-fold:

(1) Utilize our low-cost, high yielding, and scalable syntheses of sub-15 nm perovskite nanocrystals to make small fillers with maximized relative permittivity through compositional control. These small fillers will be more easily processed and dispersed in the polymer matrix than ill-defined, large fillers.

(2) Sterically mitigate nanocrystal percolation in the polyimide matrix in order to maximize the breakdown voltage (and energy density) of these first generation nanocomposites.

FY 2012 HIGHLIGHTS

We completed a thorough structural study of our as-synthesized perovskite nanocrystals using a combination of high-resolution XRD (APS, Argonne National Laboratory, beamline 11-BM) and pair distribution function analysis (APS, Argonne National Laboratory, beamline 11-ID-B). This study (published in the *Journal of the American Chemical Society*) showed that while the dielectric constant of $BaTiO_3$ nanocrystals is known to decrease with decreasing size, there are still small noncentrosymmetric domains in the sub-10 nm $BaTiO_3$ nanocrystals. One can compensate for the diminished degree of noncentrosymmetry by maximizing the dielectric constant through compositional control. As such, we demonstrated compositional with our solution synthesis method of making perovksite nanocrystals by the synthesis of compositionally complex aliovalently doped and four-cation isovalently substituted solid-solution perovskite nanocrystals. These resulted in publications in *Chemistry of Materials* and *Advanced Materials*. This library of perovskite nanocrystals can now be used for the fabrication of polymer nanocomposite capacitors.

Molecular Magnets Based on a Modular Approach: Investigation of Coupling, Anisotropy and Electronic Factors on Bistability

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Funding: $240,000

PROGRAM SCOPE

Until recently, research into the phenomenon of magnetic bistability in molecules, commonly referred to as single molecule magnets (SMMs), has focused primarily on increasing the ground-state spin value (S) to raise the thermal barrier for spin reorientation, but success has been limited. A relatively unexplored avenue to increasing the blocking temperatures of polynuclear SMMs is to incorporate early 3d and 4d/5d transition metal ions that exhibit strong spin-orbit coupling into cyanide-bridged clusters, thereby introducing anisotropy into the M_1-CN-M_2 metal-ligand bond through exchange interactions. In addition to anisotropic exchange, theory has predicted that certain combinations of metal ions in the M-CN-M' linkage should exhibit extremely strong coupling. The synthesis of new cyanide molecules guided by these premises and the assessment of their structural, electronic, and magnetic properties constitute the foundation for our DOE-funded research. Simply stated, the scope of our DOE-funded project is to design, synthesize, and fully characterize new molecular nanomagnets which differ from bulk magnetic materials. We are investigating such “quantum magnets” based on strongly anisotropic metal ions by preparing homologous families of compounds in order to gain insight into the complex interplay of metal ion, ligand, and supramolecular interactions and how they affect the properties of these materials. Our strategies are guided by theoretical predictions regarding the energies of magnetic interactions as well how the ligand field of the metal affects the zero field splitting parameter that leads to Ising (or easy axis) anisotropy.

FY 2012 HIGHLIGHTS

Two recent unpublished findings represent record-breaking results in the area of the proposed research. One discovery is that a pentanuclear molecule with Mo(III) and V(II) centers exhibits the strongest exchange coupling to date through a cyanide ligand estimated at -130 cm^{-1}. A second finding is that the small molecule $[Mn(L_{N5Me})(H_2O)]_2[MoCN)_7]\cdot 6H_2O$, which exhibits antiferromagnetic coupling between the Mo^{III} and Mn^{II} spins, is a single-molecule magnet with a blocking temperature of 3.8 K (at 1 Hz) and a barrier of ~44.1 cm^{-1}. These numbers constitute records for a cyanide-bridged SMM. Moreover, hysteresis loops with obvious steps corresponding to quantum tunneling were observed up to 3 K. This compound is a “proof-of-concept” case for a SMM composed of spin centers that engage in anisotropic magnetic coupling, and its properties confirm a long-standing debate about whether this strategy would work. This result represents a major milestone in our work.

Extracting Hot Carriers from Photoexcited Semiconductor Nanocrystals

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Funding:	$210,000

PROGRAM SCOPE

This research program addresses a fundamental question related to the use of nanomaterials in solar energy -- namely, whether semiconductor nanocrystals (NCs) can help surpass the efficiency limits, the so-called "Shockley-Queisser" limit, in conventional solar cells. In these cells, 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; this sets the solar cell efficiency at a limit of ~31%. 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%. A potential route to capture this energy is to utilize semiconductor nanocrystals. In these materials, the quasi-continuous conduction and valence bands of the bulk semiconductor become discretized due to confinement of the charge carriers. Consequently, the energy spacing between the electronic levels can be much larger than the highest phonon frequency of the lattice, creating a "phonon bottleneck" wherein hot-carrier relaxation is possible via slower multiphonon emission. For example, hot-electron lifetimes as long as ~1 ns have been observed in NCs grown by molecular beam epitaxy. In colloidal NCs, long lifetimes have been demonstrated through careful design of the nanocrystal interfaces. Due to their ability to slow electronic relaxation, semiconductor NCs can in principle enable extraction of hot carriers before they cool to the band edges, leading to more efficient solar cells.

FY 2012 HIGHLIGHTS

We have achieved the first direct and quantitative determination of hot electron relaxation dynamics in semiconductor QDs. We used femtosecond time-resolved two-photon photoemission spectroscopy to carry out a complete mapping in time- and energy-domains of hot electron relaxation and multi-exciton generation dynamics in PbSe quantum dots functionalized with 1,2-ethanedithiols. We also established graphene nano-materials as viable candidates for hot carrier chromophores. We probed hot electron injection and charge recombination dynamics for graphene quantum dots (QDs, each containing 48 fused benzene rings) anchored to the TiO_2(110) surface via carboxyl linkers. We find ultrafast hot electron injection from photoexcited graphene QDs to the TiO_2 conduction band and charge recombination dynamics that depend on the depth (and thus electron energy) of the initial injection.

Materials and Interfacial Chemistry for Next-Generation Electrical Energy Storage

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Funding:	$700,000

PROGRAM SCOPE

This project has three major emphases that enable the development of new materials and transformative advances in batteries for vehicle and stationary storage applications. First, we aim to improve the understanding and control of the fundamental processes that occur at the interfaces of the anode and cathode. Second, we focus on improving Li^+-ion diffusion in solid electrolytes with higher voltage limits. Specifically, these processes are examined with ex-situ studies of Li^+-ion transport across the electrode-electrolyte interfaces as well as in the electrodes and electrolytes. Third, we utilize low-temperature synthesis to stabilize metastable phases.

FY 2012 HIGHLIGHTS

(1) Interfaces: Introduction of M^{3+} ions into the high-voltage ($V \approx 4.75$ V vs Li^+/Li^0) spinels $Li[Ni_{0.5}Mn_{1.5}]O_4$ has been shown to reduce the Ni concentration at the particle surface, thus lowering the oxidation of the electrolyte at high charge to give longer cycle life at 55°C. Control of thermal history to confine Ni^{2+}, Mn^{4+} ordered short-range clusters provides the best cathode performance.

(2) Li-ion Diffusion: (a) By using Al particles as oxide getters, synthesis of carbon-buffered Cu_2Sb nanoparticles has demonstrated fabrication of an anode of a Li-ion battery that allows the fast charge needed for electric vehicles. (b) The concept of flow-through liquid cathodes and, with an aqueous catholyte, the use of oxide catalysts for an air cathode have been shown to be viable; but the commercially available solid Li^+ electrolyte used as a separator is not adequate. (c) As an alternative solid Li^+ electrolyte, we have developed, in the garnet system $Li_{7-x}La_3Zr_{2-x}Ta_xO_{12}$ with $\times \approx 0.6$, a Li^+ conductivity $\sigma_{Li} \approx 10^{-3}$ S cm^{-1} at room temperature. The fabrication with this compound of a mechanically robust, thin membrane is under development.

(3) Stabilization of Metastable Phases: Microwave synthesis of V-doped $LiFePO_4$ established that aliovalent V(IV)/V(III) is compensated by Fe vacancies and the solubility of V is temperature-dependent.

Spectroscopy of Charge Carriers and Traps in Field-Doped Single Crystal Organic Semiconductor

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Funding:	$180,000

PROGRAM SCOPE

This research project 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. 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. These properties have lead to the common observation of low charge carrier mobilities, e.g., in the range of 10^{-5} - 10^{-3} cm^2/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 cm^2/Vs have been observed in OFETs operating at room temperature. Outstanding questions are the following. *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?* These questions are critically important but not comprehensive, as the nature of charge carriers is known to evolve as the carrier concentration increases, due to the presence of intrinsic disorder in organic semiconductors. Thus, a complementary question is "*How does the nature of charge transport change as a function of carrier concentration?*". To answer these questions, the PIs are carrying out a collaboration that combines transport measurements with in situ spectroscopy; the new focus is on single crystal organic semiconductor field effect devices.

FY 2012 HIGHLIGHTS

We have carried out quantitative transport measurements of single crystal OFETs using ionic liquids as dielectric. In order to carry out spectroscopic and microscopic measurements on operating OFET devices, we have developed a nonlinear optical microscope to directly image the spatial distribution of charge carriers in operating organic semiconductor devices. We are also at the final stage of putting together a FTIR and NIR microscope for the spectroscopic measurements.

Optical, Electrical and Magnetic Studies of Conjugated Systems

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Funding:	$210,000

PROGRAM SCOPE

This program deals with the optical, electrical, and magnetic characterizations of π-conjugated molecules, oligomers, and polymers. For our studies we use a myriad of regular and nonlinear optical techniques, electrical measurements on active devices, and various spin injection methods. Specifically, we focus on (1) organic donor-acceptor blends for photovoltaic applications such as organic solar cells, (2) organic light emitting diodes for displays, and (3) organic spin-valve devices for magnetic-field driven switches.

FY 2012 HIGHLIGHTS

We have studied the photogeneration process in organic donor-acceptor (D-A) blends used for photovoltaic applications utilizing picoseconds transient and steady state optical techniques. We found that the charge photogeneration process in neat D-A blends is a two-step process. First, excitons are photogenerated in the donor grains; subsequently the excitons diffuse to the D-A interfaces in the film where they subsequently form charge-transfer (CT) excitons. This diffusion stage takes ~ 10 ps depending on the donor grains size in the film. In the second step, the CT excitons dissociate into polaron-pair and then to free polarons in a much slower process (up to few micro-seconds). This model may be used to gain deeper understanding on the photogeneration dynamics in a variety of D-A blends, which at present may show up to 9% solar power conversion efficiency in organic solar cells.

We also found that spin ½ additives, such as Galvinoxyl radicals, may dramatically improve the organic solar cell performance: up to ~15% for optimized cells and 300% for cells having excess acceptor concentration. This novel effect may be caused by the spin-spin interaction between the radicals and the spin ½ photogenerated polarons on the acceptors, following the formation of charge transfer excitons at the D-A interfaces. This model has been confirmed by the magneto-photocurrent method, which is sensitive to the density of the charge transfer excitons in the active layer.

The Influence of Electrolyte Structure and Electrode Morphology on the Performance of Ionic-Liquid Based Supercapacitors: A Combined Experimental and Simulation Study

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Funding:	$0.00 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

The main objective of this project is to obtain fundamental understanding of correlations between electrolyte structure, electrode morphology, and the performance of ionic liquid-based supercapacitors. The interdisciplinary team of materials scientists and engineers has utilized a combined simulation and experimental approach and focused the research in three main areas: (1) obtaining molecular-level understanding of factors influencing properties of room temperature ionic liquid (RTIL) electrolytes at electro active interfaces and in nanostructured electrodes using theory and molecular dynamics (MD) simulations, (2) designing and characterizing novel RTIL mixtures for application as electrolytes in supercapacitors, and (3) developing novel nanostructured carbon-based electrode materials and testing new electrolyte/electrode combinations for supercapacitors applications.

FY 2012 HIGHLIGHTS

(1) Molecular simulations. We showed that DC capacitance dramatically depends on the geometry of surface nanopatterning and can be used to significantly increase the energy storage of the capacitor. Molecular simulations of RTILs and nanoporous carbon-based electrodes showed a substantial increase in capacitance in subnanometer pores. We also showed that the structure of each electrode can be optimized independently depending on the structure of the intercalating counterion.

(2) Novel electrolytes. Salt mixtures have been systematically explored including: (a) salts with the same anion and same cations, but the latter have different alkyl chain lengths; (b) salts with the same anion and different cations; (c) salts with the same cations, but different anions; and (d) mixtures of different RTILs with LiTFSI. Investigation of these mixtures explored (i) the possibility of inclusion of significant amounts of salt with short alkyl chain length to improve the transport properties, (ii) how the thermal phase behavior is impacted by different cations, (iii) how mixtures of anions may enable the liquidus range of salt mixtures to be extended to low temperature, and (iv) how the inclusion of limited amounts of smaller cations may be beneficial or detrimental to the charging behavior of porous electrodes. The mixtures composition is being correlated both with properties and electrode cycling behavior to deconvolute the factors which govern device performance.

(3) RTIL-based supercapacitors with nanostructured electrodes. We have systematically studied the effect of pore/ion size on EDLC performance, particularly on power and temperature range of operation. We have shown that while small pores (close to ion size) can lead to higher capacitance, high power or low temperature operation is negatively affected, due to kinetic limitations to ion transport. Additionally, we have demonstrated that the temperature range of operation can be expanded through

the use of carbons with easily accessible surfaces (i.e., exohedral carbons such as vertically-aligned CNT forests) and through the use of eutectic RTIL mixtures with suppressed phase transitions.

Synthesis of Molecule/Polymer Based Magnetic Materials

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Funding: $237,000

PROGRAM SCOPE

The design, synthesis, characterization, and exploitation of organic-based magnetic materials and those combining magnetism with other technologically important properties (e.g., electrical, optical, pressure, and mechanical) are the research focus. These materials are important for future electronic/photonic devices, especially due to the need for earth-abundant, rare earth-free materials, reduced energy consumption, and environmentally friendlier processing and disposal. Our work will continue our successful interdisciplinary studies of ferro-/ferrimagnetic ordering in organic-based materials. This embryonic area of materials chemistry has a significant potential for technological innovation and the discovery of new phenomena.

FY 2012 HIGHLIGHTS

The reinvestigation of $M^{II}(TCNE)[C_4(CN)_8]_{1/2}$ (M=Mn, Fe) reveals that they are antiferro- not ferrimagnets. A spin-flop transition occurs at 19.5 kOe at 5 K for Mn, while Fe is a Class 1 metamagnet. Fe exhibits a constricted hysteretic behavior with a 5 K critical field of 12.6 kOe, and coercive field and remanant magnetization of 4.8 kOe and 1,850 emuOe/mol, respectively. Mn has a reversible pressure-induced transition from an antiferromagnet to a high magnetization ferrimagnet above 0.5 kbar, and in the ferrimagnetic state, T_c increases with P and is 97 K at 12.6 kbar, the magnetization increases by a thousand, and the material becomes a hard magnet with a significant remnant magnetization. This piezomagnetic transition suggests applications in transducers, sensors, and actuators.

Several new non-cubic Prussian blue analogue (PBA) magnets have been prepared, e.g., $A_2Mn[Mn\text{-}(CN)_6]$ (K, Rb, Na, $Na{\cdot}H_2O$). They have nonlinear MnCNMn linkages, and the bent cyanide bridges play a crucial role in the superexchange mechanism by increasing the coupling via shorter Mn-Mn distances and, perhaps, enhanced overlap. Hence, T_c increases as the Mn-N-C angle decreases from linearity. The magnetic structure for A = K has a non-compensated, collinear, antiparallel magnetic moments oriented along the *b* axis with a T_c of 40.6 K, and the beta critical exponent is 0.38. Layered $[NEt_4]_2[Mn_3(CN)_8]$ is a ferrimagnet at 27 K. In contrast, $[NEt_4]Mn_3(CN)_7$ has direct bonding via bridging cyanides between ferrimagnetic layers leading to antiferromagnetic coupling between the layers, and has different magnetic behavior. Thermolysis of either $[NEt_4]_2[Mn_3(CN)_8]$ or $[NEt_4][Mn_3(CN)_7]$ form antiferromagnetic $Mn(CN)_2$ (T_c =7 3 K) possessing two independent, interpenetrating diamondoid networks. The reaction of Mn^{II} and $[NMe_4]CN$ forms $[NMe_4]_2Mn^{II}{}_5(CN)_{13}$ that has a highly disordered structural motif with unusual Mn^{II} sites with a single layer motif similar to beta phase of U_3O_8, and its order as antiferromagnet at 11 K.

Design and Synthesis of Chemically and Electronically Tunable Nanoporous Organic Polymers for Use in Hydrogen Storage Applications

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Funding:	$260,000

PROGRAM SCOPE

The objective of our research was to develop porous organic polymers for use in gas storage and separation application. We have described the incorporation of borazine units bearing three different B-substituents (H, Cl, Br) as building blocks for the construction of porous networks (Borazine-Linked Polymers: BLPs) to assess the impact of pore decoration on hydrogen storage and selective gas binding. As such, we envisioned the inclusion of different halides to alter the electronic nature of the pores and the polarizability degree of the borazine building units in BLPs. We have determined the porosity of several BLPs and their gas uptake under low pressure and calculated their respective heats of adsorption. Generally, BLPs exhibited moderate surface areas and relatively high gas uptakes in comparison to porous organic polymers. We have also reported several studies on the use of a new class of porous organic polymers named Benzimidazole-Linked Polymers (BILPs) in gas storage (H_2, CH_4, CO_2) and separation applications (CO_2/CH_4, CO_2/N_2). BILPs are insoluble in common organic solvents such as tetrahydrofuran, dimethylformamide, dichloromethane, methanol, and acetone; they also remain intact upon washing with a 2M aqueous solution of HCl or NaOH, which reflects their high chemical stability. BILPs are among the best known organic polymers for hydrogen storage under ambient pressure and low temperature conditions and also exhibit excellent selectivities for CO_2/CH_4 and CO_2/N_2, which makes this class of material promising for gas storage application and CO_2 capture and separation.

FY 2012 HIGHLIGHTS

We have described the synthesis and use of BLPs and BILPs in small gas storage and separation studies in several publications. Most notably, our work on BILPs and their performance in CO_2/CH_4 was highlighted by the American Chemical Society during a press release entitled “More economical way to produce cleaner, hotter natural gas” during the ACS 243rd National Meeting in San Diego on March 26, 2012. BILPs are among the best performing porous adsorbents for CO_2 capture and separation and, due to their remarkable physicochemical stability, are very interesting candidates for membrane fabrication for use in gas separation applications.

Molecular and Nanoscale Engineering of High Efficiency Excitonic Solar Cells

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Funding: $380,000

PROGRAM SCOPE

By coupling tailored materials design of both organic and inorganic materials closely with device measurements and optical spectroscopy, we propose to use new materials to harvest more of the solar spectrum while generating larger cell voltages by uncovering the fundamental factors such as energy level offsets, relative dielectric constants, interfacial chemistry, and morphology that control relative branching ratios between geminate recombination and free carrier generation at a range of model donor/acceptor interfaces. These studies will identify the design rules and fundamental performance limits for new OPV and hybrid organic/inorganic materials. Specific objectives include (1) developing new p-type polymers with tailored energy level offsets and different morphologies to systematically explore the effects of energetics and morphology on recombination loss in polymer/fullerene systems; (2) exploring new n-type polymers with a range of energy levels, optical bandgaps, and carrier mobilities to enable investigation of effects of energetics and morphology on device performance and recombination loss in polymer/polymer BHJ solar cells for comparison with fullerene acceptors; and (3) designing and studying new hybrid inorganic quantum dot/polymer combinations for extending the response of solution-processable solar cell materials into the near and mid-IR, while exploring the role of acceptor dielectric constant and surface chemistry.

FY 2012 HIGHLIGHTS

We have demonstrated that the reduced photocurrent yield in a derivatized fullerene blend was partly due to the suppression of hole transfer due to reduced driving force. This work addressed a key fundamental question of the driving force needed to support exciton dissociation and subsequent charge escape from the donor/acceptor interface in polymer/fullerene blends, focusing on the less-studied topic of hole back transfer from the fullerene. We also showed that a state energy picture of the charge transfer driving force could better predict photocurrent generation than a HOMO/LUMO offset picture. To accomplish this, we studied photoinduced charge transfer and device performance in blends of several fullerene acceptors with a new donor polymer with a large oxidation potential prepared in the group. Suppressed hole transfer from fullerene excitons is a potentially important consideration for materials design and device engineering of organic solar cells relying on fullerene absorption.

Polymer/quantum dot bulk heterojunctions have been known since the 1990s. However, the mechanism of photocurrent generation remains an open question in many systems. We have now produced direct spectroscopic evidence that photoinduced hole transfer takes place from PbS quantum dots to a semiconducting polymer host. We obtained this result using our workhorse photoinduced absorption (PIA) spectroscopy experiment to study blends of the PDTPQx polymer (prepared by Jenekhe) with PbS quantum dots (made by Ginger). The resulting PIA spectra show a clear spectral fingerprint of an identical polymer polaron resulting from either direct visible excitation of the polymer, or selective infrared excitation of the PbS quantum dots.

Fundamental Studies of Charge Transfer in Nanoscale Heterostructures of Earth-Abundant Semiconductors for Solar Energy Conversion

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Funding:	$660,000

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 2012 HIGHLIGHTS

We developed nanomaterials of several earth-abundant semiconductors and their nanoscale heterostructures. We built on our success in synthesizing epitaxial heterostructures of PbSe quantum dots (QDs) with α-Fe_2O_3 nanowires (NWs) and expanded to other systems. We synthesized and structurally characterized the epitaxial heterostructures of PbSe and PbS QDs on TiO_2 and SnO_2 nanorods (NRs) grown on FTO substrates via solution synthesis. We also tried to grow CdSe and CdS QDs onto TiO_2 NRs but only had limited success. We also have investigated and found organic ligands to effectively stabilize CdSe and other chalcogenide QDs against photocorrosion and to improve stability of CdSe-based solar devices by using ligands that will remove the resulting holes from the QDs. We have also developed a facile method for converting α-$FeF_3 \cdot 3H_2O$ NWs to porous semiconducting α-Fe_2O_3 NWs of high aspect-ratio on FTO substrates via a simple thermal treatment in air. Photoelectrochemical (PEC) investigations of these nanostructured photoelectrodes showed promising photocurrent and photovoltage without intentional doping. Furthermore, a facile post-growth Ti-doping or Zr-doping treatment was developed to significantly improve the photocurrent.

We also advanced the capabilities of the multiresonant coherent multidimensional spectroscopy (CMDS) methods. In particular, we implemented capabilities for isolating specific coherence pathways, measuring the ultrafast coherent dynamics, or probing electronic states in the visible and ultraviolet parts of the spectra. The system now uses 35 femtosecond pulses that are used to create two independently tunable excitation pulses from the ultraviolet to the infrared. A third pulse was also created using a white light generation process. The time delays between pulses were also extended so we can now follow dynamics over the six orders of magnitude from femtoseconds to nanoseconds. These capabilities were then mated to different experimental systems so we could perform pump-probe, transient absorption, transient grating, photon-echo, sum frequency generation as well as the wide variety of multiresonant CMDS experiments. These new capabilities have provided some very important insights into the ultrafast excitonic dynamics occurring in QDs. In particular, the original excitonic states created by an excitation pulse relax on 50-100 fsec time scales to states with narrower Bohr radii that don't sense the quantum confinement. There is further relaxation on time scales of 150-500 fsec to surface trapped excitonic states.

ARRA Chemical Frustration: A Design Principle for the Discovery of New Complex Alloy and Intermetallic Phases

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

PROGRAM SCOPE

Intermetallic phases form a broad family of compounds of immense importance to materials science. They adopt a diverse array of crystal structures that has yet to be accounted for with chemical bonding concepts. The absence of a theoretical framework for understanding and predicting the preferred crystal structures of these phases is a limiting factor in the design of new metallic materials with useful physical properties, such as hydrogen storage, catalysis, and superconductivity. In this project, a joint theoretical and experimental approach is taken to develop one approach for understanding the driving forces underlying the crystal structures of these phases, and to gain some degree of control over these structures. The approach draws a common theme that has been perceived in some of the most complex intermetallic crystal structures: structural complexity can be linked to a tension between mutually exclusive bonding types coexisting in the same phase. In this project, new compounds will be sought out by inducing such tension through the selection of combinations of elements with inherent conflicts in the preferred types of chemical bonding and atomic packing. Changes in the ratios of these elements are then employed to shift the balance of power in these conflicts. The resulting phases will be studied with structural analysis and quantum mechanical calculations aimed at examining how their crystal structures accommodate tension between competing bonding types. This approach to the design of new intermetallic structures has the potential of facilitating the development of new alloys for a wide range of applications.

This project will focus on the achievement of three main objectives: (1) the synthesis and characterization of new chemical frustration-driven intermetallic phases, (2) the theoretical analysis of the consequences of this frustration on the electronic structures of these phases, and (3) the merging of these experimental and theoretical results into guidelines for harnessing chemical frustration in the design of new phases. These objectives will be pursued over five years. Objectives 1 and 2 will be targeted during years 1-3, with the focus shifting to objective 3 during years 4 and 5. During all five years, the achievement of these goals will be approached through solid state synthesis, structural characterization, and theoretical calculations; and for years 2-5, these research activities will expand to include materials properties measurements.

FY 2012 HIGHLIGHTS

We have developed a new theoretical approach, the mu3-acidity model, for understanding the stability and structural features of transition metal-based intermetallic phases. In this approach, the Method of moments as applied to DFT-calibrated Hueckel calculations (a technique we highlighted during FY 2012 in a perspective article) is used to classify the transition metal elements into acids and bases, with the reactions between them to form intermetallics then being understood as acid/base neutralization processes. These insights will help in the design of chemically-frustrated systems for synthetic exploration. We also completed our analysis of a new carbometalate in the Gd-Fe-C system: Gd13Fe10C13. This phase is unique for its Fe2C4 units containing unusually short Fe-Fe contacts of ~2.37 Å. Theoretical analysis indicated that Fe-Fe multiple bonding may be occurring at these contacts.

DOE National Laboratories

Innovative and Complex Metal-Rich Materials

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Funding:	$760,000

PROGRAM SCOPE

This project strives to (1) uncover and ultimately design new families of intermetallic phases, (2) understand the factors that stabilize both new and known phases by combining exploratory synthesis and temperature-dependent structure determinations with electronic structure theory, and (3) establish structure-property relationships for complex metal-rich materials as related to practical as well as fundamental issues, e.g., thermoelectric, magnetocaloric, catalytic, and magnetic behavior. Targeted compound classes include, but are not limited to, Zintl-type, cluster-based, Hume-Rothery-type, polar intermetallics, quasicrystalline and approximant phases, as well as complex metallic alloys. Also, elements of the 5th and 6th period transition elements, viz., Pd, Pt, Ag, and Au, represent a significant focus because not only do few binary intermetallic compounds exist with these elements, but relativistic enhancements of valence electron binding energies, especially for Pt and Au, contribute to the stabilities of their compounds.

FY 2012 HIGHLIGHTS

A plethora of new and noteworthy families of polar intermetallic compounds appear when members of the heavier 5th period and 6th period transition metals are combined with early, active metals like alkali metals, alkaline-earth metals, and even rare-earth metals. Substantial recent developments leading to new quasicrystals and approximants include (1) discovery and characterization of the first icosahedral quasicrystal containing sodium, $Na_{13}Au_{12}Ga_{15}$; (2) systematic identification of numerous approximants in the Na-Au-T (T = Ga, Ge, Sn) systems; (3) discovery of a novel Mackay-type quasicrystal approximant in the Mg-Pd-Zn system; and (4) discovery of a decagonal quasicrystal approximant of Ca_6PtCd_{11}. Striking magnetic coupling and atomic distributions have been identified in complex Co-Zn systems and Y_3MnAu_5 with a very unusual intergrown structure. In addition, novel polar intermetallic chemistry includes

(1) discovery, characterization, and electron/hole doping studies in $BaAu_2Sn_2$ and $BaAuSn_2$; (2) discovery of a new layered phase in the Li-Ca-Mg-Si system featuring layers of icosahedra and half-icosahedra; (3) commensurate and incommensurate cation distributions in the tunnels of homologous intermetallic phases in the Na-Au-Zn and Na-Au-Ga systems; and (4) novel cluster condensation in Ca-Cd-Pt and Er-Pd-Sb phases.

Solid-State NMR of Complex Materials

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Funding:	$725,000

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:

- Nanocomposites, in particular biological (e.g., bone) and related bioinspired materials (in collaboration with the FWP on Bioinspired Materials), by ^{31}P, ^{1}H, and ^{13}C NMR.
- 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.
- Proton conductors, such as the Nafion fuel-cell membrane, by ^{19}F and ^{13}C NMR.
- Thermoelectric tellurides, characterizing by ^{125}Te NMR the distribution of dopants, charge-carrier concentrations, and local symmetry, and correlate with transport properties measured in-house.
- NMR of carbon materials as used in supercapacitor electrodes, and nanodiamond, by ^{13}C NMR.
- General NMR pulse-sequence development to provide new structural information.
- Simulations of NMR parameters and scattering curves for extracting the maximum information content from the available data.

FY 2012 HIGHLIGHTS

Rare Earth Atoms Make the Best Better - Small addition of rare earth element improves conversion of heat to electricity. Research in this program, using ^{125}Te NMR and X-ray diffraction, has shown that small amounts (1-2%) of rare-earth dysprosium atoms distort the structure of a high-performance thermoelectric alloy based on GeTe, and change the way heat and electrical charges move through the material. The thermoelectric figure of merit was increased by >15%, to near-record values. The enhancement is attributed to selective scattering of undesirable lower-energy charge carriers by dysprosium, allowing the higher-energy to move preferentially through the material. [E.M. Levin et al., *Adv. Funct. Mater.* 22, 2766 (2012)]

Mutated Plants May Make Better Biofuels. As part of an interdisciplinary team, researchers in this program used ^{13}C NMR to show that cellulose microfibril crystallinity is reduced by mutating C-terminal transmembrane residues of the cellulose synthase enzyme. This is promising for genetic engineering of plants to enable easier extraction of cellulose as an energy source. [D. M. Harris et al., *Proc. Natl. Acad. Sci. USA* 109, 4098 (2012)]

Directed Energy Interactions with Surfaces

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Funding:	$520,000

PROGRAM SCOPE

The Directed Energy Interactions with Surfaces program focuses on fundamental studies of the interaction energy sources such as ions and photons with materials. The knowledge gained enables us to develop world-class elemental, isotopic, and molecular analysis instruments for nanoscale materials characterization, which in turn enables us to answer questions about new or previously unobservable phenomena, and to develop and study new materials. The program consists of two integrated activities: (1) understanding of energetic ion- and laser-solid interactions, and (2) the development of world-class instrumentation. The interaction of directed energy sources with surfaces provides the basis for modifying, patterning, and analyzing materials. This program investigates these interactions using unique methods developed in our laboratory that push the frontiers of surface analysis to lower concentrations, smaller dimensions, and higher precision, both for analytical applications involving complex materials structures, and for studies of the mechanisms of directed energy interactions with materials.

FY 2012 HIGHLIGHTS

We studied ion-solid interactions in terms of the sputtered flux and the effects of irradiation on the solid. Ion bombardment initiates a collision cascade that leads to sputtering of mostly neutral species. Laser ionization of these species separates the sputtering and ionization events and provides insights into the mechanism of each separately. We sputtered uranium oxide with medium energy (15-25 keV) atomic and cluster ions. Increasing the mass and nuclearity of the projectile increases the proportion of molecules in the flux and decreases the proportion of atoms. Our calculations showed that higher primary ion nuclearity leads to shallower penetration depths and enhanced sputtering rates, distributing the primary ion energy over a greater number of sputtered species rather than being absorbed in the solid. Each sputtered species has lower internal energy and experiences less fragmentation. These results are important in developing effective analytical techniques and in designing methods that use the sputtered flux as a basis for materials synthesis or modification.

We developed low energy (0.25 – 0.5 keV) sputtering to decrease the damage done by primary ions in order to increase the depth resolution of ion sputtering. The beam gently removes material with minimal damage or mixing, exposing fresh surface to be analyzed with ultralow-dose medium energy ions. This dual-beam approach enabled us to achieve a depth resolution of 0.4 nm (~2 atomic layers). Because the low energy milling beam does not roughen the material, we were able to use a Mixing-

Roughness-Information model to visualize buried interfaces in solid materials (alternating 4 nm layers of MgO and ZnO) and to characterize their intrinsic roughness (due either to the synthesis method or to post-synthesis processing) at arbitrary depths.

Energy and Fuels from Multifunctional Electrochemical Interfaces

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Funding:	$1,160,000

PROGRAM SCOPE

We propose an interdisciplinary, atomic/molecular level approach, integrating both experimental- and computational-based methodologies to design, synthesize, and characterize electrochemical interfaces for efficient transformation of chemical energy into electricity and/or to utilize the energy of electrons for the synthesis of chemicals that can be stored and re-used. The proposal describes a science-based approach to developing new materials, and interfaces with specific focus on the electrocatalytic reactions involving the water cycle ($H_2 + O_2 \leftrightarrow H_2O$) and the carbon cycle ($C_xH_yO_z + O_2 \leftrightarrow x\ CO_2 + y/2\ H_2O$). These two cycles are expected to constitute the core building blocks for an efficient, green and viable energy landscape required for the design and synthesis of multi-functional electrochemical interfaces with specifically tailored properties. A two-fold strategy is proposed. The first centers on the design of novel energy efficient multi-functional materials with tailored properties, such as metals and metal alloys, complex oxides, metal-metal oxides, and chemically modified electrodes. The second strategy centers on the understanding and design of multi-functional double layers, a “solution-phase” of electrochemical interfaces established in the vicinity of catalytic materials. To develop a multi-scale capability for tailoring electrochemical interfaces, we will rely on the research facilities at Argonne National Laboratory and a set of unique, state-of-the-art, ex-situ and in-situ surface-sensitive probes. The synergy obtained from the combination of experimental and computational methods, together with the application of knowledge, concepts, and tools developed in this program, will lead to a new generation of multi-functional interfaces for efficient energy conversion and fuel production.

FY 2012 HIGHLIGHTS

Controlled arrangement of nanometer scale $Ni(OH)_2$ clusters on platinum surfaces manifests a factor of 10 activity increase in catalyzing the hydrogen production relative to state-of-the-art metal and metal oxide catalysts. In a bi-functional effect, the edges of the $Ni(OH)_2$ clusters promote the dissociation of water leading to the production of hydrogen on the nearby Pt surfaces. This work has been published [*Science* 334 (2011) 1256] and highlighted on the Office of Science’s webpage of the DOE as a significant contribution to the research field.

A new generation of catalysts for the oxygen evolution reaction in alkaline environments has been developed. By monitoring activity trends on 3d-hydroxyoxide catalysts, it was found that the rate of the oxygen evolution reaction on NiOOH and CoOOH is 2-fold higher than on the state-of-the-art Ru-based catalysts. This work has been published [*Nature Materials* 11 (2012) 550].

Nanostructured Carbon Materials

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Funding:	$825,000

PROGRAM SCOPE

The world-leading capabilities at Argonne for nanodiamond and cluster synthesis, in situ characterization, and state-of-the-art computational materials design will be utilized in an integrated program for development of functionalized nanocarbon-based materials with controlled electrochemical reactivity. Among the unique properties of ultrananocrystalline diamond is its large electrochemical window, inert surface, and increased conductivity via doping that makes it very attractive as an electrode material. These properties make it ideal to develop it as a support for small metal and metal oxide clusters that we have recently shown to be highly active and selective for catalytic reactions. We have unique capabilities to synthesize small metal and metal oxide clusters of specific size and composition. The proposed program has the goal of interfacing well-defined clusters and UNCD to make new hybrid materials with tailored electrocatalytic properties and using heterogeneous catalysis knowledge as a guide. A key part of this program will be the use of ex situ and in situ characterization and computational capabilities to both understand the properties of the new nanocarbon materials as well as perform screening to find optimal candidate clusters to be used on the nanocarbon supports for the electrocatalysis. The focus will be on key electrochemical reactions for fuel production and energy storage.

FY 2012 HIGHLIGHTS

The composition and stability of oxidized cobalt subnanometer clusters composed of four metal atoms supported on ultrananocrystalline diamond (UNCD) and alumina surfaces were studied using a combination of grazing-incidence x-ray absorption near-edge spectroscopy (GIXANES), grazing incidence small angle x-ray scattering (GISAXS), and density functional calculations. The study revealed partially oxidized subnanometer cobalt clusters upon exposure to air, with similarity in the total degree of oxidation on both supports and resistance to agglomeration at elevated temperatures. DFT calculations of cluster binding to model surfaces for UNCD indicate that the stability of the cobalt oxide clusters on UNCD is the result of electrostatic and dispersive interactions for the pristine hydrogen-terminated surfaces and covalent bonding between the cluster and defect sites on the surfaces. Tests of various size subnanometer clusters supported on ultrananocrystralline diamond were performed for water splitting. Results from repeated cycles indicate a promising stable cluster-diamond hybrid material for use under electrocatalytic conditions. The results show an interesting cluster size dependence that is explained by density functional calculations of the reaction mechanisms on the differing reaction sites on the different size clusters. An analysis of the ex situ x-ray data has provided evidence that the clusters remain unchanged after the electrocatalytic cycling.

Rational Synthesis of Superconductors

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

PROGRAM SCOPE

We propose a focused materials synthesis program to investigate superconducting behavior in pnictide and intermetallic systems exhibiting competing interactions and in narrow gap semiconductors. The project pursues a multi-faceted approach that combines the rational design of novel materials with structural and electronic 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. Namely, we plan to create materials with a high degree of structural and compositional freedom and chemical/electronic complexity with which to investigate (1) density-wave instabilities (spin and charge) and their suppression through chemical doping in order to generate superconductivity that may emerge from phase competition, and (2) 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 2012 HIGHLIGHTS

For alkali iron selenides, which have been in a debate because the identity of superconducting phase is still unclear, we prepared high-quality $K_xFe_{2-y}Se_2$ samples and found four distinct phases: semiconducting $K_2Fe_4Se_5$, a metallic superconducting phase $K_xFe_2Se_2$ with x ranging in 0.38 - 0.58, an insulator $KFe_{1.6}Se_2$ with no vacancy ordering, and an oxidized phase $K_{0.51}Fe_{0.70}Se$ that forms the PbClF structure upon exposure to moisture. This coexistence of metallic and semiconducting phases explains a broad maximum in resistivity around 100 K. Further studies to understand the solubility of excess Fe in the $K_xFe_{2-y}Se_2$ structure have also been in progress to maximize the fraction of superconducting $K_xFe_2Se_2$.

From a systematic investigation of $Ba_{1-x}K_xFe_2As_2$ using high quality samples we prepared for the entire x range, a new phase diagram was constructed with a detailed magnetic and structural phase diagram that displays a narrower phase coexistence region than that given in previous reports. Neutron diffraction and magnetization data indicate magnetic and structural transitions are coincident with first-order transitions. Our results confirmed the importance of obtaining precise structural parameters across the whole phase diagram as a way of providing insight into the nature of the phase competition that underlies iron-based superconductivity.

Chemical and Mechanical Properties of Surfaces, Interfaces and Nanostructures Program

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Funding:	$1,460,000

PROGRAM SCOPE

The purpose of this program is to carry out atomic level studies of surfaces and nanomaterials, focusing on chemical, mechanical, and physical properties: structure, diffusion, reactions, catalysis, friction, and wear. The molecular level knowledge generated by the proposed studies will help the development of novel catalysts with higher activity and selectivity, and the discovery of novel materials of nanometer dimensions with unique mechanical, chemical, and optical properties and of materials with improved mechanical properties of adhesion, friction, and wear. The results from this project benefit many energy based industries, including chemical, petroleum, mechanical, electronics, solar energy, etc. To accomplish these goals, we utilize materials in the form of single crystals, biointerfaces, and nanoparticles. We develop methods for making nanocrystals with narrow particle size distribution and well-defined shape. We develop new instrumentation for the characterization of our materials under the widest possible range of operating conditions: under vacuum, at ambient pressure, and at the solid-liquid interface. These include sum frequency generation (SFG) surface vibrational spectroscopy, high pressure scanning tunneling microscopy (HPSTM), and ambient pressure x-ray photoelectron spectroscopy (APXPS).

FY 2012 HIGHLIGHTS

Using HPSTM and AP-XPS, we discovered that under 1 Torr of oxygen, the stepped Pt(557) single crystal surfaces undergo restructuring into nanometer wide clusters, a process of great relevance in the catalytic properties of Pt. In our efforts to determine the molecular scale mechanism of catalytic reactions, we determined the dissociation pathways of NH3 on Ru(0001) and the structure of its product species (NH2, NH,N) adsorbed on the surface.

We have solved an old puzzle of the structure of water wetting layers on metals, finding that they form both commensurate and incommensurate structures in the first layer. We discovered that water can split graphene by breaking C-C bonds along the defect boundary lines, even at 90 K. We discovered a new friction anisotropy phenomenon of graphene layers on Si wafers, which is due to the formation of anisotropic ripples along zig-zag directions of the C atoms. We also found that water intercalates between mica and graphene as well as between mica and silicon oxide, which greatly influences chemical and mechanic properties.

We have developed synthetic methods for producing metal nanoparticles (Au, Ag, Pt, and bimetallic systems PtPd, PtRh, PtNi, and PtCo) of controlled sizes (1-10 nm), shapes, and symmetry and studied the shape-dependent gas-phase catalytic selectivity.

Inorganic/Organic Nanocomposites Program

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Students:	3 Postdoctoral Fellow(s), 8 Graduate(s), 0 Undergraduate(s)
Funding:	$1,253,000

PROGRAM SCOPE

This activity is directed towards organic/inorganic nanocomposite materials. The goals are to design functional materials and make them by parallel and hierarchical self-assembly. In particular, we seek to develop wet chemical processes by which organic/inorganic composites can be created with a high degree of control on many length scales simultaneously. By developing a comprehensive ability to design, assemble, and pattern organic/inorganic composites and control their interfaces, it will be possible to prepare complex materials in which several microscopic processes are independently and simultaneously optimized. A range of functional materials can be created in this manner, with applications in energy conversion, mechanical composites, and optical/electrical devices. Special attention is directed to solar cells.

FY 2012 HIGHLIGHTS

We have successfully developed approaches to (1) modulate the carrier concentration by two orders of magnitude from their native values in nanocrystal thin films in a systematic, incremental and reversible fashion; and (2) achieve 1-D, 2-D, and 3-D ordered arrays of nanoparticles using block copolymer-based supramolecules in bulk and in thin films. Furthermore, we have established the capability to systematically study the electronic transport properties of oligoconductive polymers using conductive AFM. In the next period, we strive to functionalize nanoparticles with conjugated organic ligands with tailored lengths, HOMO-LUMO levels and binding groups; investigate self-assemblies of conductive ligand decorated nanoparticles; and systematically characterize the electronic properties at the particle/ligand interface and interparticle communication. Experimental studies will be guided and augmented by the strong theoretical component in the team.

Nuclear Magnetic Resonance Program

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Sr. Investigator(s):	
Students:	5 Postdoctoral Fellow(s), 9 Graduate(s), 0 Undergraduate(s)
Funding:	$1,151,472

PROGRAM SCOPE

The Nuclear Magnetic Resonance (NMR) Program addresses the development of new concepts and techniques in NMR and magnetic resonance imaging (MRI). The continuing goal of our research program is to dramatically broaden their range of applications and capabilities through unconventional methodological, technological, and chemical innovations. Specifically, we seek to enhance the capability and applicability of magnetic resonance for the investigation of molecular structure and organization in systems from natural materials to artificial, functionalized nanomaterials. The study of quantum spins interacting with each other and with other degrees of freedom also requires the development of new theoretical and experimental methods, one outcome of which is the design and fabrication of novel, next-generation NMR and MRI instrumentation. Finally, we apply these novel methods and instrumentation to exemplary materials research applications in collaboration with other LBNL programs, outside laboratories and industry.

FY 2012 HIGHLIGHTS

We made significant progress towards each of the specific aims of our work proposal. First, in the category of “Optical Detection and Encoding of NMR and MRI,” our work has included the combination of hyperpolarization techniques, including those based on parahydrogen, with zero-field NMR and optical detection, the further development of NMR J-spectroscopy in the limit of a small, finite magnetic field, and a demonstration of its analytical potential in a library of small molecules. We have developed an optically-detected NMR platform to perform the kinds of spin relaxation-based NMR measurements that are essential in industry and have demonstrated their specific applications in petrophysics and geophysics. Finally, we have developed novel magnetometers based on diamond NV- centers for microscale and nanoscale MRI. Our work has resulted in methods to develop diamond substrates of the desired isotopic composition using CVD and ion implantation, the development of a microfluidic diamond magnetometer whose sensitivity is ~10 fold better than the current state of the art, and several investigations of mechanisms of spin polarization transfer between hyperpolarized diamond spins and bulk nuclei for sensitivity-enhancement.

In the pursuit of our second aim, “Enhancing the Sensitivity of NMR and MRI for Molecular Sensing in Complex Mixtures,” we demonstrated that molecular imaging sensors can be designed from a combinatorial library screen and targeted to small molecule analytes; we have also combined xenon-based molecular sensing with microfluidics using “remote detection.”

In the area of “Microfabricated NMR and MRI for Portable Chemical and Systems Analysis,” our principal result has been the successful fabrication and operation of a microfabricated xenon polarizer.

Finally, in the area of “Unconventional NMR and MRI in Materials Science and the Carbon Cycle,” we pursued new analytical applications in materials including microreactors and polymer monoliths. We also introduced a technique to visualize combustion processes in opaque objects in three-dimensional detail. The NMR program remains a robust source of technology transfer, generating significant intellectual property, licenses, and technology transfer-related awards such as the R&D 100.

Physical Chemistry of Inorganic Nanostructures Program

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Funding:	$1,155,000

PROGRAM SCOPE

This program emphasizes the fundamental science of synthesis and preparation of the basic building blocks of nanomaterials, as well as the characterization of their physical processes. The program consists of three subtasks: physical chemistry of semiconductor nanocrystals, fundamentals of semiconductor nanowires, and microscopy investigations of nanostructured materials. The first subtask develops the science of colloidal inorganic nanocrystals, and reliable and robust methods to prepare uniform nanocrystals of different materials, including semiconductors, metals, and magnetic materials, and investigates fundamental optical, electrical, structural, and thermodynamic properties of nanocrystals. The second subtask develops the science and technology of a broad spectrum of 1-dimensional inorganic semiconducting nanostructures or nanowires. The final subtask develops state-of-the-art optical characterization microscopies and ultrafast dynamics measurements that provide higher spatial, spectroscopic, and time resolutions than are afforded by conventional techniques.

FY 2012 HIGHLIGHTS

We have successfully developed new synthesis strategies based on ion exchange reactions and facet control to obtain nanocrystals of greatly improved quality. Examples include highly monodisperse and crystalline covalent lattices such as III-V semiconductor nanocrystals (Beberwyck et al., *JACS* 2012), highly luminescent ionic nanocrystals (Jain et al., *Angew. Chem.* 2012), and semiconductor nanorods tipped with selective faceted metals (Schlicke et al., *Angew. Chem.* 2012). Furthermore, we have shown that our new design of graphene liquid cell TEM technique enables the first in situ observation of solution phase nanoparticle growth at atomic resolution (Yuk et al., *Science* 2012). Other state-of-the-art optical and electron microscopic techniques have been employed to probe the fundamental aspects of band gaps (Segets et al., *ACS Nano* 2012), ligand effects (Cordones at el., *JACS* 2012), and ferroelectric ordering (Polking et al., *Nature Materials* 2012) for a wide range of nanocrystals. In the next period, we envision further development of these newly emergent characterization techniques and mechanistic study of the nanocrystal growth mechanism that can together provide understanding of the fabrication of functional nanocrystals devices.

Giant Nanocrystal Quantum Dots: Controlling Charge Recombination Processes for High-Efficiency Solid-State Lighting

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Funding:	$651,000

PROGRAM SCOPE

Solid-state lighting (SSL) has the potential to replace less efficient and robust lighting technologies. However, a fundamental understanding of the processes that impact the conversion of electricity into light is still needed to fully realize this potential. As recently observed (DOE/EERE 2011 Joint Roundtable), nanostructures can serve as platforms for understanding such fundamental processes, but also as solutions to realizing control over exciton→photon conversion pathways. In our work, we study and develop a new class of optical nanomaterial—the "giant" nanocrystal quantum dot (g-NQD). g-NQDs are thick-shell core/shell NQDs that exhibit unique photo-physical/chemical behavior (non-blinking, non-photobleaching, suppressed non-radiative Auger recombination, large Stokes shift, surface-independent emission). Through three research goals, we aim to establish g-NQDs as functional "building blocks" for SSL with combined attributes of high-efficiency, robustness, low-cost, and color tunability: (1) establish quantitative g-NQD "structure-function" relationships for fully predictable/consistent performance and new g-NQD development, (2) understand/control exciton →photon conversion pathways via strategic manipulation of intrinsic and extrinsic g-NQD properties, and (3) demonstrate performance-benchmarking in light-emitting devices.

FY 2012 HIGHLIGHTS

Research Goal 1. We determined the individual and collective effects of multiple reaction parameters on g-NQD shape and crystalline phase, and the relationship between these structural features and optical properties. This understanding allowed us to improve QY to ~50% for ultra-thick shell g-NQDs and blinking suppression to 100% [Y. Ghosh et al., *J. Am. Chem. Soc.*, 134, 9634 (2012)]. We also demonstrated that the g-NQD approach can be applied to new compositions with the first demonstration of non-blinking near-infrared NQDs [A. M. Dennis et al., *Nano Lett.*, 12, 5545 (2012)].

Research Goal 2. To understand the effect of electronic structure on g-NQD properties, we synthesized a range of InP/II-VI core/shell thick-shell systems that afforded tunable carrier confinement. Our optical studies revealed that the spatial separation of electrons/holes gives rise to strong suppression of Auger recombination, extreme tunability in photoluminescence (500-1100 nm), and (above) suppression of blinking in the near-IR spectral range.

We developed a novel single-nanocrystal spectroelectrochemistry approach to determine the role of charging in blinking suppression of g-NQDs [C. Galland et al., *Nature Comm.*, 3. 908 (2012)]. We have also explored g-NQD photon emission statistics in the presence of silver "nanoflake" films. We demonstrated for the first time that the interaction with localized plasmons can transform the photon emission statistics of g-NQDs from photon-antibunching to strong photon-bunching.

Research Goal 3. We demonstrated the unique attributes of g-NQDs as 'building blocks' for either direct-charge-injection LEDs or down-conversion devices [B. N. Pal et al. *Nano Lett.*, 12, 331 (2012); J. Kundu et al. *Nano Lett.*, 12, 1965 (2012)].

Hydroxide Conducting Systems Fuel Cells

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Funding:	$130,000

PROGRAM SCOPE

The purpose of this work is to provide a fundamental understanding of the stability and performance of hydroxide conducting materials, and from this understanding, develop novel materials to help enable a hydrogen based economy. The approach of this project has been to use theory, modeling and experimental tools to gain a fundamental understanding of the mechanisms of ion transport and chemical degradation in hydroxide conducting systems. Our approach consists of two primary components: (1) molecular dynamics modeling, to identify the fundamental principles and patterns of hydroxide and carbonate mobility and of molecular degradation mechanisms of the cations; and (2) synthesis and stability of known and novel organic cations, to determine decomposition mechanisms and rates and means of modifying cations for improved stability.

FY 2012 HIGHLIGHTS

We focused on unusual ylide rearrangements, a general (albeit slow) degradation pathway in these materials. Isotopic labeling studies with ^{13}C and D labels allow us to elucidate the mechanism of both the neopentyl trimethylammonium degradation as well as to determine the propensity for benzyl trimethylammonium cations to also degrade via ylide mechanisms. We also investigated cations that show increased stability. To date, diamine and ether containing ammonium ions have shown such increased stability, and determining the mechanism of degradation should allow us to find the optimal design for this class of ammonium ion. It appears that the improved stability of these species may arise from the electron donating effects of the heteroatom substituents.

Hydroxide Conductors for Energy Conversion Devices

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Funding: $400,000

PROGRAM SCOPE

The goal of this project is to understand the stability and degradation mechanisms of cations in the presence of hydroxide with a focus on those cations that can be tethered into membranes for energy conversion devices. We have used chemical and thermal degradation studies of target cations to elucidate degradation mechanisms and rates and have correlated our experimental results with computational studies. Recently, advances in anion exchange membrane (AEM) durability that have been reported are in reasonable agreement with our experimental and computational studies of cation durability, suggesting current AEMs may have the durability required for some limited applications. Further advances will likely be required for widespread adoption. Our continuing work will focus on improved stability using advanced tetherable cations with nitrogen, phosphorous, sulfur, and carbon centers or cobaltocenium; comparisions between cations in solution and in polymers; and the electrochemical impact of ions on catalysis. These studies will help lead to improved AEMs helping enable next generation energy conversion devices.

FY 2012 HIGHLIGHTS

We have enhanced our understanding significantly of ammonium cations and developed and applied unique tools to their degradation mechanisms and rates. Additionally, we have refined our computational models and correlated these results with experimental degradation studies. In the past year, we have focused on nitrogen charge centered cations. Our detailed studies included substituted trimethyl ammonium (TMA^+) cations investigating both the importance of the number of β-H's for alkyl substituted TMA^+ and the importance of electron donation and withdrawing on benzyl TMA^+. A primary finding from our studies on substituted TMA^+ is that strategies employed to date have had only minimal impact on the reaction barriers observed, with only modest improvements in stability. To date, the best durability obtained for an ammonium cation in our tests has been a threefold increase in stability relative to $BTMA^+$ with an ether-linked substituted TMA^+. In order to seek further improved stability, we are now exploring cations beyond nitrogen charge centered cations.

Fundamental Charge Transfer Processes in Stable Free-Radical Organic Polymer Systems

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Funding:	$600,000

PROGRAM SCOPE

Polymers with stable pendant radical groups have emerged as a unique class of electroactive materials that are emerging as potentially deployable materials for energy storage, transport, and conversion. These polymers facilitate remarkably rapid, efficient, and reversible multi-step charge transfer processes. However, a lack of basic understanding of structure-property relationships in most organic charge-transfer solids results in a knowledge gap that impedes rational efforts to design improved organic materials for energy storage applications. One key deficiency is that the current knowledge base is inadequate when it comes to understanding charge mobility within the solid-state organics. The focus of this project is to advance the fundamental understanding of the mechanism(s) of electron transfer and ion transport, along with associated interfacial barriers, that impact the redox processes of organic free-radical polymeric microsystems. The lack of an advanced understanding of the mechanism(s) involved in electron or ion transfer for these polymeric materials hinders rational design efforts to improve the electroactive properties of radical containing polymers. The effort in this project is an integrated, three-pronged approach consisting of chemical synthesis, electrochemistry, and theoretical modeling of new functional materials that are aimed at establishing which physical, chemical, and electrochemical principles control electron and ion transfer inside the radical polymer matrices and across polymer-electrolyte interfaces. The goal is to advance directed synthesis of new materials with tailored properties, to test theoretical models and advance understanding of charge transfer in multivariate organic redox systems. This work has cross-cutting 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 2012 HIGHLIGHTS

In the synthetic thrust, the scientists synthesized gram quantities of four different organic nitroxide radical species with different amounts of radical content. Experimentally, both the spectroscopists and electrochemists completed a series of preliminary experiments. The initial photoluminescence studies commenced in FY 2012, looking at the effect of the nitroxide level content on a luminescence marker. Additionally, the initial electrochemical characterization was performed on standard nitroxide radical materials in efforts to optimize conductivity of binder/carbon/active material inks. Finally, the theoreticians explored the accuracy of different electronic structure approaches for radical and multi-radical entities, evaluated different levels of electronic structure calculations on example materials (e.g., TEMPO-methacralate), and completed a comprehensive literature search to identify promising approaches for multi-radical containing oligomers.

Materials and Interfacial Chemistry for Next Generation Electrical Energy Storage

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Funding:	$800,000

PROGRAM SCOPE

Electrochemical energy storage systems, specifically batteries, are critically needed to effectively use clean, abundant renewable sources of energy and effectively integrating these sources into the electrical grid. Furthermore, the development of electric vehicles of the future requires greatly improved batteries. Today's battery technologies fall far short of meeting future needs for transportation and grid application. The overarching goal of this project focuses on understanding and controlling fundamental processes that occur at the interfaces of the anode and cathode and the limitations of electrolytes. To achieve this goal, we will address (1) understanding and controlling processes that occur at the anode, (2) understanding and controlling mechanisms that occur at the cathode, (3) understanding voltage limits imposed by the electrolyte, and (4) design of new inorganic or polymer/ceramic composite electrolytes that allow the use of alternative, high capacity cathodes. Thus, this program addresses opportunities for transformative advances in batteries for vehicle and stationary storage applications.

This project is partnered with a university project led by John Goodenough (University of Texas, Austin). The primary focus of the ORNL research effort lies in characterization and electrolytes.

FY 2012 HIGHLIGHTS

A novel approach based on small angle neutron scattering enables the observation of electrochemical processes during the cycling of high capacity lithium ion batteries. Better understanding of processes such as solid-electrolyte interphase (SEI) formation have been of great interest to overcome performance limitations of batteries for vehicle and grid applications. Changes in neutron scattering intensity associated with mesopore ordering show the processes of SEI formation and lithium intercalation. In addition, neutron diffraction has been used as part of a collaborative effort between UT-Austin and ORNL to better understand the atomic structure of the high-voltage doped spinel oxides LiMn1.5Ni0.5−xMxO4 (M = Cr, Fe, and Ga; $0 \le x \le 0.08$).

Sulfone-based electrolytes are promising for the development of high-voltage based lithium-ion batteries as electrolytes with electrochemical windows greater than 5 V. We computed the electrochemical windows for experimentally tested sulfone electrolytes by different levels of theory in combination with various solvation models. A similar computational method was utilized to guide the experimental investigation of the structure-function relationship of electrolytes based on ionic liquids.

Polymer-Based Multicomponent Materials

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Funding:	$1,985,000

PROGRAM SCOPE

The central goal of this research is to develop a fundamental understanding of chemical and physical processes that can be used to design and control the interfaces, dispersion, and ordering in multi-component polymer systems. Two research themes form the basis of the proposed research. The first seeks to correlate structure-property relationships in polymer-nanoparticle mixtures with molecular-level interfacial interactions, while the second involves the correlation of molecular architecture and orienting fields to the morphology and dynamics of multi-block copolymer materials, including both neat block copolymers and those containing discrete nanoparticles. The nature of the interface impacts the ease of processing, mechanical properties, dynamics and morphology, and the optical and electronic properties of these promising materials; and thus understanding and controlling the interactions between polymers and nanoparticles, as well as between nanodomains in phase-separated block polymers, is vital. Such understanding will provide new materials with superior properties and functions that can address many DOE challenges, such as organic photovoltaics, fuel cell membranes, and stronger light-weight materials that result in energy savings. To fully understand and exploit these novel materials, a comprehensive interdisciplinary approach will be employed that includes tailored synthesis with precise nanoscale control, state-of-the-art characterization techniques (including neutron scattering and dielectric spectroscopy), and a wide range of theoretical tools.

FY 2012 HIGHLIGHTS

A microscopic, quantitative, first principles statistical dynamical theory at the level of intermolecular forces for the violation of the Stokes-Einstein (SE) diffusion law of a spherical nanoparticle in entangled and unentangled polymer melts has been developed. The nanoscale non-hydrodynamic friction coefficient is related to liquid structure and polymer melt collective density fluctuation dynamics. A rich dependence of the non-hydrodynamic diffusivity and SE violation ratio on particle size and polymer chain length, tube diameter, degree of entanglement, temperature, and interfacial attractions is predicted. Entanglement effects are found to be the origin of orders of magnitude increase of nanoparticle diffusion; while unentangled melts show little enhancement, predictions are in good accord with recent experiments.

We discuss the new dimension to manipulate the morphology of block copolymers—use of charged blocks. Targeted-self-assembly controlled by this new parameter endows block copolymers with even broader technological applications. Nanophase separation into well-defined morphologies has been experimentally developed and theoretically calculated for neutral polymers. However, incorporation of charges into a block copolymer dramatically changes the rules of phase separation. Charged states and electrostatic interactions significantly affect morphological behavior on a molecular level, which creates a new dimension for manipulating phase behavior as desired. Also, an emerging marriage of ionic liquids or poly(ionic liquids) with block copolymers endows soft matter with broad applications in areas such as catalysis, gas separation media, and energy.

Diamondoid Science and Applications

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Funding:	$792,000

PROGRAM SCOPE

This program focuses on diamondoids as a new class of functional nanomaterials based upon their unique electronic, mechanical, and structural properties. This FWP includes all phases of diamondoid investigation, from diamondoid isolation from petroleum, chemical functionalization, and molecular assembly, as well as electronic, optical, and theoretical characterization. We have currently focused on four areas of research: synthesis, electronic properties, thin film growth, and nitrogen-vacancy centers. This naturally requires the broad expertise and collaboration between a number of investigators to successfully tackle these problems. This approach has yielded fruit, enabling synthesis of a number of new compounds, and exploration of their structural and electronic properties. In particular, the ability of these materials to control the flow of electrons and emitted electron energy at the molecular level is an exciting direction for mastering energy flow at the nanoscale.

FY 2012 HIGHLIGHTS

Based on the unique high van der Waals, low-entropy nature of the diamondoid molecules, our team was able to demonstrate the longest sp-3 C-C bonds ever reported (Nature, 2011). The strong van der Waals interactions between diamondoids supplanted some of the normal C-C bond energy, enabling the bond to extend significantly from the normal 1.54 Å to 1.72 Å, and extraordinarily large increase that was stable up to 300°C. This type of interaction may lead to a new approach to designing molecules and catalysts taking advantage of the ‘weak’ interactions in a way that was not possible without diamondoids. We also made a significant step forward in x-ray PEEM imaging. Normally X-PEEM is limited by the chromatic dispersion (energy spread) of the electrons emitted by the sample. Only a few facilities have developed the equipment necessary to achieve ~25 nm resolution with x-ray excitation. We demonstrated that a single monolayer of diamondoids applied by simply dunking the sample in to a diamondoid thiol solution improved the X-PEEM resolution to <10 nm, without the use of any additional correction equipment. This opens up the ability to do high resolution X-PEEM imaging on standard PEEM microscopes all over the world with very simple sample preparation. This result stems from the remarkable ability of diamondoids to strongly scatter and relax incident electrons to the diamondoid conduction band.

We made progress in developing robust diamondoid enhanced field-emission guns required for commercial applications. In addition, we were able to find new methods for using diamondoids as seed particles for bulk diamond growth. Our new method enables us to synthesize small (~5-20 nm) diamond nanoparticles at high density.

Two-Dimensional Chalcogenide Nanomaterials

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Funding:	$500,000

PROGRAM SCOPE

The goal of this project is to build a cutting-edge interdisciplinary program on two-dimensional (2D) chalcogenide (O, S, Se, Te) nanomaterials, with emphasis on their design, growth, and basic electronic and electrochemical properties. This effort lays the foundation for broad impact in their development for energy and electronics applications, via understanding and control of charge transfer and storage, as well as developing new synthetic tools for ‘materials by design’. While 2D chalcogenides have been investigated historically, recent research indicates that numerous new scientific and technological opportunities emerge. Based on their proven record in this area, the two Co-PI’s (Cui and Hwang) will integrate their activities synergistically to develop 2D nanomaterials research.

To reach this long-term vision, this proposal outlines three specific fundamental aims and associated research to be conducted within three years:

(1) Design and synthesize 2D chalcogenide nanomaterials with atomic and nanoscale control of composition, size, morphology, and orientation.

(2) Tune the electron density of 2D nanomaterials and create new artificial electronic bands by chemical, electrochemical, and oxidative methods.

(3) Establish the relationship between structural, electronic, and electrochemical properties by integration of nanostructure characterization using electron/ion transport, in-situ transmission electron/x-ray microscopy, and optical measurements.

Mechanical Behavior and Radiation Effects

Institutions Receiving Grants

Dynamic Fracture in Dealloying Induced Stress Corrosion Cracking	
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Funding:	$131,000

PROGRAM SCOPE

This research program examines the role of unstable dynamic fracture processes in dealloying induced stress-corrosion cracking of face-centered cubic alloys. This form of stress corrosion cracking is particularly relevant in energy conversion systems (both nuclear and fossil fuel) as many failures in alloys such as austenitic stainless steel and nickel-based systems 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 un-dealloyed parent phase alloy. Thus, 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. High-speed (10^6 frames s^{-1}) digital photography is used to measure crack velocity as a function of the porosity length scale and electrochemical potential. The other set of experiments referred to as *intergranular crack injection* involves forming a porous dealloyed layer of prescribed thickness and ligament size and loading the system while observing it with the high-speed camera. The tunable set of experimental parameters includes the nanoporous gold length scale (5-40 nm), thickness of the dealloyed layer (10-3000 nm), and the electrochemical potential (0.1-1.5 V, NHE). The results of crack injection experiments are characterized using the dual-beam focused ion beam/scanning electron microscope and aberration corrected scanning transmission electron microscopy. Additionally, orientation-imaging microscopy is used to ascertain if there are any particular grain boundary types that are more susceptible than others to cracking.

FY 2012 HIGHLIGHTS

This program began in August 2012. Xiing Chen is a new graduate student in Sieradzki's group assigned to this project. She is currently learning about the experimental protocols that we developed for these experiments while performing some preliminary research for this project. She is working with and learning from three senior students in the group: Shaofeng Sun, Qing Chen, and Xiaoqian Li. This involves sample preparation techniques and use of the high-speed camera. Additionally, she is receiving training on the dual-beam focused ion beam/scanning electron microscope and aberration-corrected scanning transmission electron microscope. We have started to examine dynamic fracture in monolithic nanoporous gold in electrolyte under an applied electrochemical potential. At this stage, the results are too preliminary to report.

Fracture Mechanisms and Fatigue of Magnetic Shape-Memory Alloys

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Funding: $75,000

PROGRAM SCOPE

The goal of this project is to develop a fundamental understanding of the mechanisms of fracture and failure of magnetic shape-memory alloys (MSMAs) under high-cycle magneto-mechanical loading, and to improve the fatigue life by suppressing the formation and propagation of cracks. The overarching hypothesis originates from the assumption that the interaction of course, orthogonal (i.e., intersecting) twins, nucleate and propagate cracks during high-cycle actuation of MSMAs. To avoid fracture and failure, twins must not intersect.

FY 2012 HIGHLIGHTS

We designed and built a rotary magneto-mechanical fatigue testing apparatus for the systematic testing of up to 60 cylindrical samples at a field frequency between 7 Hz and 22 Hz. We further upgraded a linear testing device with closed-loop control capabilities.

Ni-Mn-Ga single crystals were produced with a modified Bridgman design. Mechanical polishing and electropolishing yielded a surface roughness of 20 nm. Preliminary fatigue experiments with the rotary magneto-mechanical fatigue testing apparatus demonstrated the formation of cracks at twin intersections.

Understanding and Controlling Toughening Mechanisms in Nanotube Reinforced Ceramic Coatings

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Funding: $220,000

PROGRAM SCOPE

The performance of many ceramic coatings is limited by low fracture toughness. Nanoreinforcements in these materials can provide substantial toughness improvements, based in part on previous research at Brown University which provides the first direct evidence that ceramics can be toughened with multiwalled carbon nanotubes (MWNTs). The research in this project builds on this existing expertise and focuses primarily on developing fundamental understanding of toughening mechanisms. These investigations consist of well-integrated experimental and theoretical / computational efforts.

The experiments use ceramics reinforced with nanotubes to obtain detailed information on the relationships between materials characteristics and mechanical behavior (primarily toughness). In MWNT-reinforced materials, the influences of the internal carbon structure (primarily graphene ordering), nanotube dimensions (diameter and wall thickness), the nanotube-matrix interface (roughness and bonding), and residual stresses on the composite properties are not well understood. This range of material characteristics is being varied systematically using a variety of processing methods. Silicon nitride and oxycarbide matrices are used for most of these investigations, in part because we have already demonstrated that MWNT reinforced silicon nitride coatings exhibit excellent mechanical properties. Electron microscopy and detailed mechanical testing are being used to evaluate the structure and performance of these materials. This thorough study of MWNT-reinforced silicon nitride has expanded our understanding of toughening mechanisms, and we expect the general knowledge obtained from this work to be broadly applicable to a wide range of other ceramic nanocomposites.

The modeling efforts are closely coupled with the experiments described above to gain understanding of deformation and interfacial sliding on the nanoscale. Atomistic modeling of realistic composite unit cells using chemically reliable input has been used to understand deformation mechanisms, and provides quantitative predictions about toughening as a function of the reinforcement dimensions (diameter, wall thickness, interface roughness) and structure (graphene ordering, density). Modeling at the mesoscale uses these nanoscale studies to inform parametric models, and has allowed us to correlate nanoscale material properties with behavior at larger length scales. This provides detailed understanding of how features of the material, at atomistic and microstructural scales, lead to the observed macroscopic properties.

Investigation of Radiation Damage Tolerance in Interface-Containing Metallic Nano Structures

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Funding:	$150,000

PROGRAM SCOPE

The proposed work seeks to conduct a basic study by applying experimental and computational methods to obtain quantitative influence of helium sink strength and proximity on helium bubble nucleation and growth in He-irradiated nano-scale metallic structures, and the ensuing deformation mechanisms and mechanical properties. The proposed nano-scale in-situ tension and compression experiments on low-energy He-irradiated samples combined with site-specific microstructural characterization and modeling efforts present a powerful method for gaining this understanding. 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.

FY 2012 HIGHLIGHTS

(1) Helium ions were implanted at 200 keV into 100 nm-diameter Cu/Fe nanotensile samples, each containing a single bicrystalline interface. The implantation led to the formation of 1–2 nanometer

diameter, ≈ 5 nm-spaced helium bubbles concentrated at the boundary and within ≈ 50 nm of the interface. In-situ uniaxial tension experiments revealed that the irradiated pillars had higher yield strengths by a factor of ≈ 2.5 and a higher UTS by 60% than the unirradiated ones, while retaining comparable ductility and without the appearance of brittle fracture. The hardening of implanted pillars is attributed to dispersion-strengthening in the Cu constituent of the sample. This is supported by the reasonable agreement between the mean He bubble spacing calculated by the Friedel–Kroupa–Hirsch hardening relation for weak obstacles and TEM analysis. The irradiation did not appear to alter the failure mechanism. These observations may be explained, in part, by the non-orthogonally oriented morphology of the interface, with the local interfacial regions oriented for shear deformation under prescribed loading carrying plastic strain prior to failure. The absence of brittle failure in He-irradiated metals is likely due to the inability of the small He bubbles to serve as sufficient stress concentrators for cracking. These results shed light on the mechanical response and fracture behavior of a single interface and its role in absorbing He. Further examination of a controlled number of interfaces can determine the contribution of each interface to the improvement in radiation tolerance and resolve the effect of sink proximity on absorbing He.

(2) We developed a fabrication methodology of 120 nm-diameter, 500–600 nm-tall, < 111 > -oriented single crystalline Cu nanopillars, which were uniformly implanted with 0.35°æ 0.05 at% of He. Uniaxial nanocompression experiments revealed that their yield strengths were ~ 1.2 GPa, ~ 30% higher than the yield strengths of the unimplanted, asfabricated pillars with the same dimensions. The stress-strain data of the implanted pillars exhibited shorter and more frequent strain bursts, as well as notable strain hardening with a hardening slope of 3.52°æ 0.82 GPa. The substantial irradiation hardening effect at ~ 100 nm scale is in stark contrast with a previous report on proton-irradiated Cu nanopillars. Such a discrepancy can be rationalized in terms of the difference in the interplay between the type of irradiation-induced defects and the spacing between the single-arm dislocation sources. In contrast with previous studies on the compressive properties of irradiated metallic nanocrystals, samples in our work were made without the use of FIB, and hence were free from the FIB-induced damage, which facilitated a much cleaner experiment. This study sheds light on the fundamental understanding of the deformation mechanism of irradiated metallic nanocrystals, and has important implications for the interplay between irradiation-induced defects and the external sample dimensions at the nanoscale.

Energetics of Radiation Tolerant Nanoceramics

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Funding: $153,000

PROGRAM SCOPE

The development of efficient radiation shielding is a critical issue in the design of nuclear plants. Nanomaterials emerged as strong candidates to enable a new generation of radiation barriers with nanoceramic coatings, nanoparticles dispersed in metallic matrices, or even large nanoceramics parts. The lack of reliable data on the thermodynamic properties of nanomaterials makes it extremely difficult to predict and fully exploit nanomaterials properties as radiation shielding devices. The goal of this project is to investigate nanomaterials with potential interest for nuclear components [the aluminate based spinels (MAl_2O_4, M = Mg, Ni, or Zn) and zirconia based materials (ZrO_2 doped with Mg, Y, or Ca)] and establish the relationship between composition, thermodynamics, and radiation resistance, aiming to enable a fine selection of nanomaterials with enhanced performance. Moreover, we will exploit the achieved knowledge to design a new nanocomposite ceramic capable of withstanding high radiation exposition by using elements of interface engineering.

FY 2012 HIGHLIGHTS

One graduate student and one post-doc have been trained in the manipulation and manufacturing of nanoceramics, in particular fabrication of nanoparticles with high processing qualities. Moreover, they were introduced to calorimetric techniques and how to use those techniques to assess the thermodynamics of the fabricated nanoceramics. As scientific results, we have successfully established the synthesis route for nano-spinels using a co-precipitation technique. This is a great achievement as the methods to create those precursors for nanostructured dense ceramics had not been established before. We have also determined the interface energetics of Y doped zirconia materials, establishing a novel trend on the nanoscale phase diagrams. These works have resulted in two publications in high-impact journals, one submitted paper, and presentations in international and national conferences.

Mechanical Behavior in Ceramics with Unusual Thermal-Mechanical Properties

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Funding:	$120,000

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, negative coefficient of thermal expansion (CTE), and negative compressibility, 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 desired 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 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 propose a combination of activities that encompass synthesis and processing to control structures, atomistic modeling to predict and understand structures, and characterization to study mechanical behavior. As a longer-term aim, the PIs will extend this study to other materials that exhibit unusual thermal-mechanical properties, including the enstatites ($MSiO_3$), where M may be Mg, Fe or Ca, and lanthanum niobate ($LaNbO_4$) which exhibits a negative linear compressibility.

FY 2012 HIGHLIGHTS

It was discovered that small amounts of Zn (as small as 0.1 percent by mol) reverse the sign of the coefficient of thermal expansion of β-eucryptite from negative to slightly positive. The presence of Zn also significantly mitigates microcracking that occurs during thermal cycling of eucryptite. It is hypothesized that Zn disrupts the Li ordering in β-eucryptite, thereby altering the thermal expansion behavior.

A nanoindentation technique recently developed to examine incipient plasticity was applied to examine the initial stages of the pressure induced phase transformation from β- to ε-eucryptite. The activation volume measured by this technique is on the order of the tetrahedra that comprise the β-eucryptite crystal structure, revealing that the transformation likely initiates via distortion and rotation of silica and/or alumina tetrahedra. Atomistic modeling has not been completed at this time to verify that the tetrahedra movements control the transformation during pressure application, but simulations of irradiation show interesting behavior. Deformations under irradiation are associated with alumina (not silica) tetrahedral; and a significant relaxation of these deformations may occur once the irradiation is stopped, even under relatively high irradiation dosages. The combination of these simulations and the experimental results is enabling the development of a complete description of the thermomechanical behavior of eucryptite.

The Coupling Between Interfacial Charge and Mechanical Deformation at High Temperatures in Ceramics

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Funding:	$150,000

PROGRAM SCOPE

The goal of this project is to understand the fundamental atomistic mechanisms underlying electro-chemical-mechanical phenomena, for example, the deformation and sintering of ceramics at high temperatures under the influence of an applied electric field. In traditional experiments and models, the chemical potential of the atomic species at grain boundaries is related to the applied stress, which then drives atom transport leading to deformation and sintering. Our unique objective is to consider how applied field can be included in a unified theory of electrochemomechanical properties. Often ceramics harbor a space charge at interfaces. The interaction between the applied fields and these local charges is being investigated. The experimental work is being carried out by applying the electrical field with a pair of electrodes directly to specimens and then studying how the field and the current flowing through the specimen change the deformation and sintering kinetics. Recent experiments with yttria stabilized zirconia and other ceramics have identified two regimes of behavior: Type A and Type B. In the first case the applied fields are low and the main effect of the field is to reduce the rate of grain growth. At higher fields, Type B behavior is seen where there is a sudden increase in diffusive transport accompanied by a large increase in electronic conductivity. This effect is so intense that zirconia, which usually required several hours at ~1400°C to sinter, can be consolidated to full density in mere seconds at temperatures that are well below 1000°C. This finding has opened up new questions of scientific enquiry such as

(1) what is the mechanism that can explain both an increase in electrical conductivity, which is normally controlled by the fastest moving charge species, and an increase in mass transport, which depends on the slowest moving charge species; (2) what is the role of Joule heating in this process; (3) what is the effect of the electric field on microstructure evolution and grain growth; and (4) is there an evidence for defect generation under the applied field that can explain the highly enhanced transport kinetics.

FY 2012 HIGHLIGHTS

We are pursuing the hypothesis that Type B behavior may be explained by the nucleation of Frenkel pairs, or interstitial-vacancy pairs. The concept is that the applied field can ionize the interstitial and vacancies rendering them neutral with respect to the lattice, and at the same time creating electron-hole pairs. The charge neutral defects can induce deformation (for example, by the vacancies migrating to interfaces under compressive and the interstitials to interfaces under tensile tractions), while the electron-hole pairs can produce electrical current in the external circuit. One prediction from this hypothesis is that the electron-hole pairs may also recombine to emit photons. Indeed we have measured strong photoemission, in the (visible) 500nm to 780nm range, that accompanies Type B phenomena.

Deformed Materials: Toward a Theory of Materials Morphology Dynamics

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Funding:	$272,727

PROGRAM SCOPE

Our group studies materials under external loading using two different approaches. First, we explore the behavior of a minimal continuum model of dislocation dynamics that forms striking cell-wall structures consistent with recent fractal analyses of experiments. We are particularly interested in *cellular structures* formed in crystals as they are deformed; our theoretical model forms self-similar, fractal patterns qualitatively similar to those seen experimentally. Second, we apply methods of statistical physics to understand brittle fracture and dislocation avalanches. In fracture, we are interested in the fluctuations of how things fail, both the distribution of strengths of a disordered material and the distribution of precursor events foreshadowing the rupture. We have a long history of DOE-supported work in avalanches and crackling noise, and recent experiments showing that the bending of metals is mediated by avalanches is a wonderful place to test our theories.

FY 2012 HIGHLIGHTS

The highlight of the last grant period would have to be our cover story in the October 25 issue of *Nature* on the 'Avalanche Oscillator.' A collaboration with Dimiduk's experimental group, we studied the crackling noise (dislocation avalanches) he found when crushing nickel nanopillars. We discovered a new route to emergent scale invariance, where slow creep-like relaxation leads to a gradual increase in avalanche sizes, until a large event resets the system far from criticality (back to small avalanches). We prepared a *Physical Review Letter* in the last year on rare event prediction for fracture; we find that the Weibull distribution used by engineers does a poor job of predicting the likelihood of a weak sample in our simulations and an alternative method works much better. (Inerestingly, the engineer's method is closely related to renormalization-group techniques we use to study continuous transitions, and our proposed method draws on the theory of abrupt phase transitions.) We also have a PRE on avalanche shapes and avalanches viewed through windows, a paper in *Computing in Science and Engineering* on analogies between dislocation dynamics and turbulence, and a *Physical Review Letter* on avalanche events near voltages where insulators turn to metals—analogies to lightning bolts.

Understanding Microplasticity Processes Related to Fatigue Damage using High Energy X-Rays and a Crystal-Based Modeling Formulation

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Funding:	$250,000

PROGRAM SCOPE

The overall goal of this project is to understand fatigue crack initiation in polycrystalline metallic alloys using both experiments and simulations. We have developed experimental methods based on high energy x-ray diffraction to monitor the evolution of individual crystal stresses and structure evolution during cyclic loading of copper specimens. The model is a finite element representation of the in situ experiment—a virtual diffractometer—that produces diffracted intensities that can be compared directly to the experimental results. The diffracted intensity is closely linked to crystal-scale plasticity associated with fatigue crack initiation in copper. We can use the structure-based model to systematically investigate hypotheses related to initiation.

FY 2012 HIGHLIGHTS

We completed the first version of our virtual diffractometer and compared the results from diffraction experiments conducted on a copper alloy (OMC). The diffraction patterns from the simulation compared well with the experimental results. The model gave us the ability to vary relevant attributes of the polycrystalline material to understand their effect. We found that the spot evolution associated with the diffracted intensity from individual grains is closely linked to crystal-scale plasticity and is driven by the evolution of the intergrain misorientation distribution. A paper summarizing this effort was accepted with minor revisions. We also conducted cyclic experiments on the OMC copper to begin to understand the evolving material state leading to fatigue crack initiation.

Deformation of Spinodally-Formed Nanostructured Two-Phase B2/L2_1 Alloys

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Funding: $150,000

PROGRAM SCOPE

The aim of this project is to understand the deformation mechanisms that control the strength of recently-discovered two-phase B2/L2_1 FeNiMnAl alloys. These alloys, which probably form via spinodal decomposition, have nanostructured (wavelength of 8-10 nm) phases aligned along <100> and have high room-temperature yield strengths of ~1450 MPa. The work focuses on three alloys, $Fe_{30}Ni_{20}Mn_{20}Al_{30}$, $Fe_{25}Ni_{25}Mn_{20}Al_{30,}$ and $Fe_{35}Ni_{15}Mn_{25}Al_{25}$. There have been few studies on the mechanical behavior of two-phase B2/L2_1 alloys. Thus, while the effort focuses on FeNiMnAl alloys, the work aims to understand the deformation behavior of B2/L2_1 alloys in general.

There are four parts to the proposed work. First, we have produced a range of microstructures by ageing at intermediate temperature, typically 823 K. Second, we are characterizing the resulting microstructures. Some specific questions that we are attempting to answer are (1) *Do the phases lose coherency upon ageing as the sizes of the phases increase?* (2) *How does the interphase interface dislocation structure depend on the phase size?* (3) *How does the degree of order of the two phases vary with temperature*? (4) *Do the compositions of the phases change significantly with temperature?* Third, we are determining how the strength depends on both temperature and strain rate for different microstructures. Fourth, we are determining the deformation mechanisms for a variety of temperatures and strain rates for different microstructures. In particular, we are determining the slip systems that operate in the B2 and in the L2_1 phase, including determining if these depend on temperature and strain rate. Coupling these observations to the microstructure and mechanical properties will enable us to model the mechanical behavior.

FY 2012 HIGHLIGHTS

We have performed detailed microstructural characterization of several FeNiMnAl alloys using transmission electron microscopy including convergent beam electron diffraction and energy dispersive X-ray spectroscopy (EDS), scanning transmission electron microscopy (STEM) including EDS and high angle annular dark field imaging, and atom probe tomography. Upon annealing the phases coarsen with very slow coarsening kinetics but do not change in chemistry, the phases remain coherent, i.e., there are no interfacial dislocations. We have determined the strength of the B2/L2_1 alloys as a function of annealing time, temperature and strain rate at elevated temperatures. Interestingly, the room temperature strength is largely independent of phase size. The alloys undergo a brittle to ductile transition with increasing temperature. Surprisingly, this transition temperature is lower for material with a coarser phase size. The L2_1 phase disorders at higher temperatures and the resulting B2 phases deform by <100> slip.

We have also examined the microstructure of two related two-phase f.c.c./B2 alloys, $Fe_{30}Ni_{20}Mn_{30}Al_{20,}$ and $Fe_{25}Ni_{25}Mn_{30}Al_{20}$. Again, surprisingly, these alloys are brittle in the very fine as-cast state, but show considerable room temperature tensile ductility when the alloys are coarsened.

Linking the Correlated Dependence of Grain Boundary Structure and Density to Defect Evolution Mechanisms during Radiation Damage

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Funding:	$300,000

PROGRAM SCOPE

Understanding and mitigating radiation damage is of paramount importance in the nuclear industry. Damage of structural materials is a major limitation to extending the lifetime of current reactors and implementation of future reactors. Although much is known about the effects, damage accumulation, information about its origin and mechanisms at the nanoscale, and how these mechanisms evolve as a function of grain boundary structure and density (i.e., grain size) is still unclear. The objective of this work is to develop an understanding of the mutual dependence of damage accumulation on atomic scale grain boundary structure and density during irradiation. 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 results in chemical inhomogeneity at the boundary. The precise role of interstitial diffusion is unknown due to the difficulty of separating interstitial and vacancy diffusion.

The objective of this research is to answer critical questions about how point defect clustering and dislocation loop formation occurs in FCC and BCC materials with a high sink density under irradiation. Specifically, it aims to characterize the effect of grain boundary character on this radiation damage accumulation. This will be accomplished using in situ microscopy methods of model pure and impure FCC and BCC materials to elucidate fundamental mechanisms of defect accumulation during irradiation. TEM samples prepared from thin films and bulk materials will be irradiated in-situ, allowing for dynamic observation and quantitative characterization of point defect and dislocation behavior under ion irradiation. The results generated will serve as a predictive tool for developing future alloys resistant to radiation damage effects, such as hardening, swelling, and radiation-induced segregation.

FY 2012 HIGHLIGHTS

Much progress was made with respect to the characterization of nanoscale grain structures, both pre- and post-irradiation, using precession diffraction in TEM. This gave rise to numerous data sets revealing recoverable nanostructures of low angle grain boundaries at increasing dose (to 20dpa Kr++). Moreover, the onset of mobile dislocation loops previously seen at 300°C in bulk Fe was seen above 400°C in the nanostructured microstructure. These findings indicate both a grain size and type dependence that will be investigated further by first varying grain boundary type.

NanoMechanics: Elasticity and Friction in Nano-Objects

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Funding:	$140,000

PROGRAM SCOPE

Nanotubes, nanowires, nanosheets, and nanobelts are gaining a large interest in the scientific community for their exciting properties, and they hold the potential to become building blocks in integrated nano-electronic and photonic circuits, nano-sensors, battery electrodes, energy harvesting nano-systems, and nano-electro-mechanical systems. While several experiments and theoretical calculations have revealed a plethora of novel phenomena in these nanostructures, many fundamental and technological questions remain open. For example, it is still unclear how the structural defects contribute to the electrical and mechanical properties of nanotubes and nanowires, and we do not know the scaling effects on the mechanical, electro-mechanical, and opto-mechanical properties of different nano-objects (N-O). Another crucial issue in nanotechnology is related to the ability to assemble nano-objects on a substrate. This issue is intimely connected with the problem of controlling frictional and adhesion forces. Friction is one of the oldest problems in Physics and yet, one of the least understood. The waste of resources resulting from our ignorance of friction and wear is estimated to be about 6% of the Gross National Product. The study of friction and adhesion in nano-objects offers the opportunity to understand at a fundamental level the energy dissipation mechanisms in friction, and at the same time to learn about the interaction forces acting between N-O/N-O and N-O/substrate for technological applications. Here, we propose a research program to study the frictional and elastic properties of N-O, such as carbon nanotubes and nanoparticles, ferroelectric and photostrictive nanostructures, and oxides nanowires, in-situ with a morphological, structural, and chemical analysis of individual N-O. The long-term goal is to understand, predict, and manipulate the interactions between atoms, molecules, and small particles, for producing nano-objects with tailored optimum mechanical, electro-mechanical, and opto-mechanical properties.

FY 2012 HIGHLIGHTS

We have shown experimentally how structural defects, surface chemistry, and possibly chirality can control the frictional properties of individual nanotubes by coupling the tubes’ transverse and longitudinal deformations during the sliding of a nano-tip on top of a nanotube. A simple analytical model has been developed, which captures very well the observed experimental behavior in the nanotubes. We also report on the measurement of the radial modulus of boron nitride nanotubes (BN-NTs) with various sizes and thicknesses. These BN-NTs are radially much stiffer than the previously reported thinner and smaller BN-NTs, and we demonstrate the key role of the morphology of the nanotubes in determining their radial rigidity.

Materials for Extreme Irradiation Environments

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Funding:	$650,000

PROGRAM SCOPE

It has long been recognized that nanostructured materials should be highly resistant to radiation damage owing to a large density of interfaces that trap point defects and He atoms. The problem with this approach, however, has been that these materials are not usually stable under irradiation, thus their overall viability for general application is limited. In our research cluster, we are exploring a novel approach to overcome this problem by investigating nanostructures that are induced by the irradiation itself and thus stable by design. We have shown that through appropriate alloying with one or several solute elements, one can gain control of the phase stability of these nanostructures. Following this approach, we are currently exploring strategies for improving materials properties, such as dimensional stability, ductility, and strength. A vital part of this research is the development of novel experimental methods for characterizing nanostructured materials and performing in situ mechanical properties tests on miniaturized specimens during elevated temperature irradiation. These experiments are employed to validate and guide our multiscale modeling efforts.

FY 2012 HIGHLIGHTS

We have developed a methodology to quantitatively assess the sink efficiency of interfaces for trapping point defects in nanostructured materials, using thin film geometry and broadening of marker layers by diffusion under irradiation. We have first applied this method to the characterization of sink efficiency of Cu/Nb interfaces by monitoring the broadening of a Au-rich marker layer in Cu using advanced electron microscopy. The results reveal that the influence of the Cu/Nb interface extends over 30 nm during irradiation at 300˚C and that the range decreases as the irradiation temperature decreases. These results have been analyzed using rate theory to extract vacancy concentration profiles as a function of the distance to the Cu/Nb interface, thus providing a first direct method to measure sink efficiency.

We have employed a new in-situ experiment to measure creep deformation of thin films during ion irradiation at elevated temperatures. We showed that nanograined Cu-W alloys exhibit good resistance to irradiation-induced creep. A new mechanism of irradiation-enhanced creep was proposed and evaluated by atomistic computer simulations. The creep mechanism derives from local relaxations within the grain boundaries as they absorb point defects produced by irradiation. The process was studied by inserting point defects into the grain boundaries and following the materials response by molecular dynamics. Calculated creep compliances are found in good agreement with those measured. The simulations, moreover, provide a direct link between irradiation-induced creep in nanocrystalline materials with radiation-induced viscous flow in amorphous materials, suggesting that grain boundaries in these materials can be treated as an amorphous phase.

In Situ Characterization of Stress-Coupled Grain Boundary Migration

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Funding:	$150,000

PROGRAM SCOPE

Stress-coupled grain boundary migration has been shown to be an active deformation mechanism in a number of nanocrystalline materials. While a fundamental understanding of this mechanism would allow for increased utilization of nanocrystalline materials for many applications (e.g., MEMS), there have been very few experimental studies done to guide and corroborate results obtained through simulations. In particular, the ability to model a material's propensity to deform via stress-coupled grain boundary migration as a function of its grain boundary character distribution would increase our ability to design with and predict the behavior of nanocrystalline materials. Ex situ tensile testing has proven to be a valuable tool in identifying materials that exhibit stress-coupled grain boundary migration but cannot provide detailed information about the microstructure as it evolves. The focus of this research program is to develop capabilities to test and characterize nanocrystalline materials in situ, allowing for characterization of individual grains and grain boundaries as the material deforms. By conducting mechanical tests in conjunction with orientation imaging microscopy, information about how grain boundaries interact with shear stresses can be obtained and compared to simulated results. Key topics of interest are how the coupling factor (amount of shear strain imposed on lattice as the grain boundary migrates) and grain boundary mobility are affected by the grain boundary character. Both SEM and TEM-based in situ tensile testing methods are being developed and employed to study these unique materials.

FY 2012 HIGHLIGHTS

A new thin film microsample fabrication technique has been developed that can produce tensile specimens of any material that can be vapor deposited. Using this method, copper films with bimodal grain size distributions were tested and shown to exhibit good strength and ductility as a result of stress-coupled grain boundary migration. A microtensile system to test thin films in a scanning electron microscope in conjunction with electron backscatter diffraction (EBSD) characterization has been developed, and initial validation tests are ongoing. By conducting thin film tensile tests using a straining holder in a transmission electron microscope, stress-coupled grain boundary migration was observed in aluminum samples.

Chemomechanics of Far-From-Equilibrium Interfaces (COFFEI)

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Funding:	$880,000

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 (1) develop models to predict chemomechanical phenomena in lithium battery and fuel cell electrodes and electrolytes, (2) characterize the relation between Li or oxygen nonstoichiometry and lattice dilation/contraction, (3) predict conditions for device failure related to rate-dependent charge/discharge rates, and (4) 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 2012 HIGHLIGHTS

Cycling-rate-independent mechanisms for electrochemical shock, including fracture driven by anisotropy and due to phase transformations in coherent, misfitting systems, were studied. Using a combination of *in operando* acoustic emission experiments and micromechanical models, we established that these cycling-rate-independent electrochemical shock mechanisms are ubiquitous among the technologically important families of lithium-storage cathode materials, including layered oxides, spinels, and olivines. Our micromechanical modeling effort has elucidated microstructure and crystal chemical design rules to mitigate these degradation mechanisms.

A combination of first-principles calculations, STM/FIB, and impedance spectroscopy measurements were applied to obtain a microscopic level understanding and control of unusually large cathodic SOFC activity enhancement at $(La,Sr)CoO_3$ (LSC_{113})/$(La,Sr)_2CoO_4$ (LSC_{214}) hetero-interfaces. Calculations showed that (LSC_{214}) (100) surfaces facilitate oxygen incorporation, with lattice strain fields playing an important role. Electronic activation of the LSC214 phase by the adjacent $(La,Sr)CoO_3$ (LSC_{113}) layers, concurrent with the anisotropically fast oxygen incorporation path, contribute to the vastly accelerated kinetics near the LSC113/214 interface. In situ synchrotron-based, ambient pressure x-ray photoelectron spectroscopy was used to study the formation of secondary phases and Sr segregation on LSC films versus powder specimens at elevated temperatures, with these changes correlated with electrode reaction kinetics. The coupling of defects and transport and chemical expansion in $Pr_xCe_{1-x}O_{2-\delta}$ was examined and correlated with altered mechanical properties. Models predicting means for minimizing chemomechanically-induced stresses were developed and tested.

nferring Grain Boundary Properties from Heterogeneous Data

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Funding: $300,000

PROGRAM SCOPE

The goal of the proposed project is to build analysis tools that infer accurate and general grain boundary (GB) crystallography-property relations with rigorously quantified uncertainty by assembling partial but complementary data readily obtainable with existing experimental and modeling methods. Such relations are challenging to establish because all methods for studying GB properties, whether through experiments or modeling, are incomplete and uncertain. The novel contribution of this project is to integrate existing modeling and experimental methods into an analysis tool that infers accurate and general GB crystallography-property relations with rigorously quantified uncertainty from a heterogeneous database of partial but complementary data.

We have selected a model problem on which to develop the analysis tools described above, namely gallium penetration into GB networks in fiber textured aluminum. Our goal, however, is for these tools to be applicable to other classes of GB-controlled properties as well. The tools we will develop may be used to guide investigations into GB crystallography-property relations by addressing questions such as:

- What is the incremental utility of specific new measurements or simulations for improving a GB crystallography-property relation? Which ones should be prioritized?
- What investigation strategy arrives at a desired level of accuracy in representing GB crystallography-property relations with least expenditure of resources?
- How can the efforts of an entire research community be evaluated, integrated, and guided to achieve maximum improvement in GB crystallography-property relations?

FY 2012 HIGHLIGHTS

This project began on September 1, 2012. To date, it has been fully staffed and work on the selected model problem has begun.

Characterization and Modeling of Deformation Induced Damage in Titanium Alloys

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Funding:	$195,000

PROGRAM SCOPE

In this program, we are continuing synergistic experimental and computational studies that examine and identify processes that cause damage nucleation at interfaces in two-phase $\alpha+\beta$ titanium (Ti) alloys. We are systematically studying one near-α phase Ti alloy (Ti-5Al-2.5Sn (wt.%), henceforth referred to as Ti525, and comparing the results with 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 temperatures. Using this knowledge to examine the deformation behavior in more complex and commercially important two-phase $\alpha+\beta$ Ti-alloy systems has yet to be performed. The program will accomplish this task by 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. The 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, biomedical, and sports and recreational industries, thereby making the program outcomes of broad practical interest.

FY 2012 HIGHLIGHTS

We have successfully characterized the deformation behavior in Ti525 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 temperatures and compared the results to single-phase α CP Ti. The tensile deformation behavior of CP Ti and Ti-5Al-2.5Sn was analyzed and compared at both 296K and 728K. Slip behavior was assessed by observing instances of surface slip visible in SEM images. Quantitative observations augmented with rigorous statistical analysis allow several conclusions to be made; Prismatic slip was the most commonly observed deformation mode in both CP Ti and Ti525. Compared with CP Ti, basal slip activity was significantly enhanced in Ti525. This can be explained by the increased c/a ratio in Ti525. In general, when the global Schmid factor of prismatic slip exceeded 0.4, it was shown to be an effective parameter to predict the activation of prismatic slip for both CP Ti and Ti525. However, this was not the case for basal slip in CP Ti because prism slip was dominant and was activated at a much lower stress than for the alloy (and hence, a much lower yield stress was observed). Temperature did not significantly affect the relative activity of the tensile deformation modes in either material. In addition to dislocation slip, twinning was also an active deformation mode in CP Ti. However, it was almost completely suppressed in Ti525. Thus, alloying led to a more balanced amount of prismatic and basal slip activity, and it reduced <c+a> activity and suppressed twinning. Dislocation slip was the primary deformation mechanism in 728K-45MPa creep of CP Ti, while dislocation slip was observed to a significantly lesser extent during 728K-250MPa creep of Ti525, where GBS was dominant.

DOE Software Innovation Center for Integrated Multi-Scale Modeling of Structural Metals

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Students:	2 Postdoctoral Fellow(s), 7 Graduate(s), 0 Undergraduate(s)
Funding:	$3,000,000

PROGRAM SCOPE

The overarching goal of this program 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/open-executable, extensible, user friendly, and efficient.

(2) Develop advanced, open source/open executable computational methods for metallic materials.

(3) Tightly couple the computational methods with advanced experimental methods for determining model inputs and 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 complex, microstructure-dependent deformation processes of magnesium alloys; fatigue, ductility, and stress-strain response of structural metals; and 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 2012 HIGHLIGHTS

The program was awarded in September 2012. The Center is in the process of interviewing and hiring staff, post-doctoral research fellows, and graduate students. Two senior staff have been hired, and plans are well along for a third staff member. Three graduate students are on the program. The faculty and senior staff meet weekly to refine the scientific and software development program plans and to define initial use cases. High performance computation and knowledge repository facilities have been scoped and quoted, and purchase orders have been issued. A new scanning electron microscopy facility for in-situ tensile and high cycle fatigue studies has been scoped and quotations are being developed.

Localized Deformation and Intergranular Fracture of Irradiated Alloys under Extreme Environmental Conditions

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Funding:	$280,000

PROGRAM SCOPE

The objective of this program is to determine, by using simulation and experimental characterization over multiple length scales, the processes by which localized deformation in irradiated materials leads to intergranular cracking in alloys in aggressive environments at high temperature. Using novel experimental techniques employing an in-situ capability, pre-determined and pre-characterized geometries for dislocation channel-grain boundary interaction, and molecular statics and molecular dynamics modeling of channel-boundary interaction, we will determine the basic processes and mechanisms by which IGC initiates in irradiated austenitic Fe-Cr-Ni alloys conducted in aggressive media at high temperature. We will determine the detailed mechanisms by which the buildup of localized stresses or strains is responsible for the initiation event. We will also determine the role of grain boundary character and solute accumulation on IG cracking. We will then be in a position to translate these findings into strategies for tailoring the response of alloys using thermal-mechanical processing and/or impurity additions. To reach our objective, four controlled purity alloys and one commercial purity alloy are used in this investigation. These alloys span a range of stacking-fault energy (15 – 61 mJ m^{-2}) and a wide range of cracking susceptibilities; 18Cr-8Ni and 18Cr-12Ni-1Si are very susceptible to cracking; 21Cr-32Ni is very resistant; and 13Cr-15Ni is moderately susceptible. Alloy 18Cr-10Ni is expected to exhibit susceptibility between the 18Cr-8Ni and the 13Cr-15Ni alloys.

FY 2012 HIGHLIGHTS

A digital image correlation technique was developed to allow measurement of the localized displacement, which in turn is converted to a nominal plastic strain in plane. Out of plane strains are determined independently via either atomic force microscopy or by laser interferometry. Elastic strains were determined from high resolution electron backscattering detection (EBSD) and were converted into Von Mises stresses providing a complete picture of elastic stresses and strains and plastic strains in the vicinity of dislocation channel–grain boundary intersections where cracking is observed to originate. The criteria controlling slip transfer through grain boundaries in irradiated metals was studied via in-situ irradiation and deformation experiments in TEM. Contrary to conventional wisdom, observations of strain contrast and density of dislocations vicinal to the grain boundary are significant, which is consistent with the premise that the transmission event is propagation and not nucleation limited. Simulations showed that a lower stacking-fault energy resulted in enhanced emission of dislocations from a grain boundary. Hydrogen segregated to the grain boundary increased the accommodation and emission of dislocations and promoted intergranular cracking.

Response of Simple, Model Systems to Extreme Conditions

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Funding:	$197,000

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. 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 2012 HIGHLIGHTS

A systematic investigation on the effect of high energy ion irradiation on the structure of a large set of simple oxides has been completed over the last year. Synchrotron x-ray diffraction data revealed that the radiation response of Ln_2O_3, with Ln = La, Nd, Sm, Gd, Ho, Tm, and Lu, is strongly dependent on the starting phase and the cation size of the material. Crystalline-to-crystalline transformations have been observed for most of the lanthanide oxides after irradiation. Such ion-induced phase transitions have been reported previously only for a limited number of materials. The effect of doping on ion-matter interactions was tested for Nb-$SrTiO_3$ (Nb: 0, 0.1 and 1 wt %). Small angle x-ray scattering and transmission electron microscopy demonstrated that track formation is insensitive to changes in electronic resistivity in this perovskite over at least seven orders of magnitude.

The combined effect of high energy ion beams, high pressure, and high temperature showed interesting material modifications in SiO_2 and GeO_2. The diameter of nanometer-sized amorphous ion tracks in quartz increase gradually with temperature to at least 640°C as evidenced by small angle x-ray scattering. A linear increase of different slope was observed for heating samples in situ and ex situ, during and after irradiation, respectively. These results, which are in contrast to commonly observed thermal annealing of damage domains, can be explained by an enhanced track-formation efficiency in SiO_2 at high temperature and related relaxation processes. Highly densified vitreous GeO_2 held at a pressure of 50 GPa could be transformed into a crystalline, disordered hexagonal phase by irradiation with energetic gold ions. In general, this high-pressure polymorph with the NiAs-structure is difficult to obtain by conventional laser heating experiments at high pressure. The interplay of radiation and high pressure provides a new route of synthesizing this metastable phase.

RECOVERY ACT - Deformation and Failure Mechanisms of Shape Memory Alloys

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Funding:	$150,000

PROGRAM SCOPE

The goal of this research is to understand the fundamental mechanics that drive the deformation and failure of shape memory alloys (SMAs). SMAs are difficult materials to characterize because of the complex phase transformations that give rise to their unique properties. These phase transformations occur across multiple length scales, one example being the martensite-austenite twinning that underlies macroscopic strain localization. Prior results on shape memory alloys have been largely qualitative (i.e., mapping phase transformations through cracked oxide coatings or surface morphology). The PI is utilizing new approaches that provide a quantitative, full-field characterization of phase transformation to conduct a comprehensive suite of experiments across multiple length scales and to tie these results to theoretical and computational modeling. These experiments probe the basic connections between length scales during phase transformation. In addition to the insights that will be gained on the fundamental mechanisms driving transformations in SMAs and their impact on SMA applications, the unique experimental methodologies that are being developed under this award are applicable to a wide range of investigations.

FY 2012 HIGHLIGHTS

Full-field deformation maps tracking phase transformation at the microstructural length scale were obtained for the first time. The massive amount of quantitative information from these first data sets are just beginning to be analyzed; currently, codes are being written to investigate parameters, including transformation Schmidt factors, martensite variant misalignments, and martensitic transformation extent in each grains, in order to examine which microstructural features play key roles in the very heterogeneous transformation we observe at the microscale. Numerous new findings have already come from these experiments. In addition to analysis, we are running tests to examine the effects of strain rate and texture, and we are working on an ultra-high resolution, single grain test to attempt to resolve individual martensite lathes. Another research thrust has been on the macroscopic characterization of the effect of texture on transformation, resulting in the discovery of a strong pattern memory in the strain accommodated by martensite under hard cyclic loading. A third research area focused on the development of transformation in thin SMA tubes under bending, where it was shown that plane sections do not remain plane locally, causing Euler-Bernoulli beam theory to over/under predict the local strain by as much as 2x; however, an appropriate mean of the lateral strain profile results in this theory being reasonable in the averaged sense.

Micro-Mechanisms and Multi-Scale Modeling of Cyclic Plastic Deformation of Magnesium Single Crystals

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PROGRAM SCOPE

Magnesium single crystals with different orientations were studied for cyclic deformation, dynamic response, and the associated microscopic mechanisms. Mechanical tests were performed at room temperature using the universal mechanical testing machines and a split Hopkinson pressure bar system. Optical microscopy, scanning electron microscopy, x-ray diffraction, electron backscatter diffraction, and high resolution transmission electron microscopy were utilized to characterize the microscopic features and the deformation mechanisms for the samples subjected to quasistatic, high strain rate dynamic/shocking, and cyclic loading conditions. The results indicated that the samples with different orientations exhibited quite different mechanical behavior and microstructural features.

For the cyclic loading condition, the following phenomena were observed. (1) The sample heavily strained and deformed for $\bar{1}014$ single crystal, and the ratcheting strain was about ten times of that for 0001 single crystal. (2) Twinning was the main deformation mechanism for 0001 single crystal; and basal slip, pyramidal slip, secondary pyramidal slip, and tension and compression twinning operated for $\bar{1}014$ single crystal.

For the dynamic loading condition, there were the following observations. (1) The mechanical properties (maximum strength, strain hardening rate, and fracture strain) increased with the increase of loading strain rate. (2) Twinning was the primary deformation mechanism for cyclic loading. (3) Non-basal dislocation operations were the dominating deformation mechanisms for quasistatic and dynamic loading, while a few twinning operations were observed for quasistatic loading.

FY 2012 HIGHLIGHTS

We performed research on magnesium single crystals under various loading conditions and demonstrated that both crystal orientation and loading condition affect the mechanical properties and microscopic deformation mechanisms. Twinning operations in some conditions can contribute to the grain refinement and change single crystals to polycrystals.

Mechanical Properties and Microstructural Evolution in Al-Li-Sc-Yb Alloys Containing Multi-Shell Nanosize Precipitates

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PROGRAM SCOPE

Experimental research is focused on the study of microstructural evolution and mechanical properties of Co-based superalloys based on the Co-Al-W system, with additions of Ni, Ti, and other transition elements. Microstructurally, nanometric precipitates are imaged by atom probe tomography, which provides detailed information about their chemical composition, size, and size distributions. Mechanical testing is performed at ambient and elevated temperature to assess the use of these superalloys as potential replacement for nickel-base superalloys.

The goal of the modeling portion of the project is to explore new alloying elements and how they affect two key properties in the use of Co-superalloys: strength and stability. This is achieved by first-principles density functional theory calculations and dislocation dynamics numerical models, which are compared and calibrated with experiments before being used to predict optimal compositions and heat-treatments.

FY 2012 HIGHLIGHTS

Four alloys have been cast, and heat-treated at various temperatures and times to create coherent nanometric precipitates, which have been imaged and chemically analyzed by atom probe tomography, and whose strengthening capability has been measured by micro-hardness. First-principles calculations and dislocation dynamics numerical models have been developed and have produced wide-ranging results. Collaborations with NASA (alloy fabrication and testing), NIST (alloy thermodynamics), and Tel Aviv University (alloying) are underway. Three articles are near submission for publication.

Transformation and Deformation Mechanisms in High Temperature Shape Memory Alloys With Nanoprecipitates

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Funding:	$224,000

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,Pt)Ti and Ni(Ti,Hf) 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 under isothermal and load biased thermal cycling conditions.

FY 2012 HIGHLIGHTS

We have achieved a breakthrough in defining the crystal structure and orientation relationships for the complex precipitate phases in Ni(Ti,Hf) alloys. These insights are being used to understand the non-monotonic variation of transformation temperature with aging in this system. The high temperature nanoindenter system has been installed and utilized to measure transformation and plastic response as a function of temperature in controlled single crystal volumes. Advances in the phase field and finite element-level modeling of the effect of the nanoprecipitates on the transformation strain and non-recoverable strain have also been achieved.

Combined Atomistic and Mesoscopic Study of Deformation of Body-Centered-Cubic Transition Metals: Effects of Alloying and Magnetism

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Funding:	$155,000

PROGRAM SCOPE

The aim of this project is to develop methodology for atomistic study of defects in body-centered-cubic transition metals that are the most important materials employed in technologies of energy production and conversion. More specifically, we aspire to advance our fundamental understanding of the deformation behavior that is, together with the fracture processes, the major failure mechanism encountered in service. The goal is to start from the electronic structure and proceed via atomistic modeling and mesoscopic models with atomistic input to constitutive relations usable at levels where atomistic approach is neither feasible nor needed. The interatomic bonding in these materials has a mixed covalent and nearly free electron character, and correct physical description of such bonding is a major task. In our research, this is treated in the framework of bond-order potentials that are based on the tight-binding method but employed in real rather than reciprocal space. These potentials are being developed for non-magnetic transition metals Mo, Ta, V, W, Nb, and Cr as well as for ferromagnetic Fe. Using these potentials, we study atomistically the glide of 1/2<111> screw dislocations with non-planar cores that control the plastic behavior of BCC metals. Using these results, we investigate the dislocation glide at finite temperatures and strain rates assuming that dislocations move via thermally activated formation of kink pairs. In order to develop this approach, the stress-dependent Peierls barrier has to be determined; and, for this purpose, we employ the nudged elastic band model that we have modified significantly so that the Peierls barrier is fully coherent with molecular statics calculations that determine the Peierls stress at 0 K. At the same time, we investigate the dislocation glide in a number of B2 intermetallic compounds by studying possible dislocation splittings in these alloys. In this way, the slip directions for different compounds have been determined; and, in the long run, we shall also develop bond-order potentials for these alloys in order to investigate directly the dislocation glide.

FY 2012 HIGHLIGHTS

We have developed a significantly modified Nudged Elastic Band Method for evaluation of the Peierls barrier of dislocations. In this approach, only a small number of atoms belongs to the elastic band while all remaining atoms are relaxed by molecular statics. The Peierls barrier evaluated in this way reproduces correctly the Peierls stress obtained in full-scale atomistic calculations, which is not the case in the previous approach.

Modulating Thermal Transport Phenomena in Nanostructures via Elastic Strain at Extreme Limits of Strength

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Funding: $150,000

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 2012 HIGHLIGHTS

We have developed a novel non-contact approach for measuring thermal conductivity of a single suspended nanowire subjected to varied strain levels, which we named *μ-Raman optomechanothermography*. We employ a microelectromechanical device to apply uniaxial tensile stress to individual silicon nanowires under a confocal μ-Raman spectroscope. Raman maps across the length and width of the nanowire at several different laser intensities enable the deconvolution of the effects of stress and temperature on the Raman spectrum. Fits of the temperature profiles at the various laser intensities along the length of the nanowire combined with estimates of absorbed laser power yield measurements of thermal conductivity corrected for contact resistance. Preliminary results of thermal conductivity as a function of stress for Si nanowires have been obtained and are being analyzed in the context of changes to phonon group velocities and relaxation lifetimes.

Plastic Strain Recovery in Nanocrystalline Materials

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PROGRAM SCOPE

Understanding the mechanisms of deformation of nanocrystalline materials is critical to the design and integration of these materials into a wide range of technological applications, including micro and nano devices for the semiconductor industry, communications, and medicine. Reduction of grain size to nanometer range leads to an enhancement of several materials properties, including yield and fracture strength and superior wear resistance. This reduction in grain size is responsible for new deformation mechanisms which are not present in coarse grained crystalline materials. One of these mechanisms is plastic strain recovery.

Even though, plastic deformation is not recoverable in coarse grained crystalline materials, very recent experiments in nanocrystalline aluminum, gold, and nickel show plastic strain recovery after unloading. This surprising effect remains unexplained but is believed to be the result of the interaction between complex processes driven by the thermally activated motion of crystalline defects with different characteristic time and length scales, such as grain boundaries and dislocations. Therefore, this unique recovery mechanism has a strong dependency on loading history, temperature, mean grain size, and grain size distribution. These effects are strongly correlated and cannot be studied independently.

Numerical simulation of plastic strain recovery in nanocrystalline metals is a particularly challenging case of multiscale modeling that requires resolution of the small length scales involved while capturing the long time scales inherent to the recovery process. Therefore, traditional multiscale approaches where the materials behavior is divided in hierarchical length and time scales and the higher length scales are informed by averages from finer resolution ones are not a feasible approach.

To address this challenge, I propose to develop a new approach to understand the mechanisms responsible for plastic strain recovery in nanocrystalline metals capturing both short length scales and long time scales. This new approach will incorporate thermally activated recovery mechanisms into large-scale numerical simulations of deformation of nanocrystalline materials with a phase field theory of dislocations. The theory and simulations proposed in this project will provide insight regarding the interaction of crystalline defects at nanometer scales over time scales not accessible with atomistic simulations and will be a critical step toward new, more general and predictive approaches in multiscale modeling.

FY 2012 HIGHLIGHTS

Plastic strain recovery is a temperature-dependent and low-rate process. To take into account these two processes, we have coupled dislocation dynamics to a kinetic Monte Carlo algorithm. Our simulations are able to predict plastic strain recovery in polycrystalline metals and show that the strain rate depends on the applied strain and the grain size distribution. Furthermore, we calculate strain rate versus stress curves that can predict, for the first time, using dislocation dynamics stress exponents for creep deformation.

Turnable Hetero-Epitaxial Shape Memory Alloys

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PROGRAM SCOPE

Shape memory materials are used for a wide range of applications, from medicine to aerospace, due to their 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 to 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: (1) coherency limits in terms of materials and size, and (2) 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 2012 HIGHLIGHTS

The team characterized the martensitic transformation that governs shape memory in Ni-rich NiAl alloys and used this information to design a series of epitaxial heter-structures expected to exhibit low phase transformation hysteresis as compared to their constituents. Coherent integration forces the two components to share the same in-plane lattice parameters; the team used this fact to engineer the energy landscape that governs the phase transition and lower the barrier that separates the martensite and austenite phases. The approach was successfully demonstrated via large-scale molecular dynamics simulations of the proposed nanocomposites that showed the expected reduction in hysteresis.

Mechanical Properties of Materials with Nanoscale Dimensions and Microstructures

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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 the mechanical properties of crystalline materials in small volumes, as well as research on 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 was discovered a few years ago using the micropillar compression technique that we also introduced. Our work includes experiments wherein the microstructure is controlled by pre-straining and focused ion beam processing, as well as computational modeling using a dislocation dynamics code based on the ParaDis code developed at the Lawrence Livermore National Laboratory. The overall aim of this work is to determine the role that dislocations play in controlling strength at small scales.

Our study of the mechanical properties of lithiated silicon nanostructures involves the use of both nanoindentation and micropillar compression techniques to determine the elastic and plastic properties of these materials. This has included ex situ studies of the mechanical properties of both crystalline and amorphous silicon, the latter with and without lithium. We also plan to include in situ transmission electron microscopy deformation studies of these same materials. Our finite element modeling studies of the lithiation of silicon are aimed at understanding the complete disintegration that can occur in silicon electrodes during the lithiation process. In particular, this includes studies of the generation of residual stresses in these nanostructures and the associated fracture of lithiated silicon nanowires (NWs), nanotubes (NTs), and nanoparticles (NPs).

FY 2012 HIGHLIGHTS

We have developed and published a simple model that provides a rational account of why the size dependence of the strength of metallic micropillars varies from one metal to another and why BCC micropillars typically exhibit smaller size effects than comparable FCC metals. When the size-independent friction stress contribution to the strength is taken into account, the strong BCC metals with large friction stresses exhibit much smaller overall size effects than FCC metals with small friction stresses. We, with others elsewhere, have also solved to puzzle of why crystalline silicon NWs and NPs fracture at the surface during lithiation, even though compression at the surface was expected based on diffusion induced stresses. By modeling the lithiation process as the growth of an amorphous lithiated shell at the expense of a crystalline silicon core, we can account for the tensile stresses that develop at the surface during lithiation, describe the fracture that those stresses cause, and explain why fracture does not occur for sufficiently small particles. Our prediction that amorphous silicon would resist facture on lithiation has been confirmed experimentally.

Molecular-Reinforced Hybrid Glass Films with Superior Thermo-Mechanical Properties

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PROGRAM SCOPE

Hybrid glass films are composed of inorganic and organic molecular networks along with monovalent terminal groups that fundamentally affect the molecular network connectivity. While they exhibit unique electro-optical properties, a fundamental challenge is that they often exhibit poor mechanical properties due to the inherently fragile nature of the inorganic component of the molecular network and reduced glass network connectivity. Hybrids often also exhibit moisture-assisted fracture behavior due to the nucleophilic sensitivity of siloxane and other moisture sensitive bonds almost ubiquitously present.

Our current DOE program has focused on developing the fundamental materials science to realize advanced hybrid glasses with improved mechanical properties together with mitigating moisture-assisted fracture behavior.

FY 2012 HIGHLIGHTS

We investigated the cohesive fracture properties of ceramic-like amorphous hydrogenated a-SiC:H hybrid films and showed that films with non-stoichiometric compositions exhibited markedly increased cohesive fracture energy. This was due to unexpected crack-tip plasticity due to the presence of carbon chains. This offers a promising approach to toughen hybrids.

We then demonstrated that such hybrid films with thicknesses of only 10s of nanometers could be used to toughen mechanically fragile thin-film structures. At these film thicknesses, metal films would not have been effective and polymers would have been too soft. This is the first time that such significant toughening by adjacent layer plasticity has been achieved at such small nanometer dimensions.

Using atmospheric plasma deposition and a newly developed high temperature precursor delivery system, we showed how dense transparent hybrid organosilicate films could be deposited onto plastic substrates at room temperature. We also showed how graded hybrid films could be produced that exhibited markedly increased resistance to moisture-assisted cracking, producing a new strategy for increasing the adhesion of interfaces.

Finally, we investigated the very low cohesion values of hybrid phase separated polymer:fullerene bulk heterojunction layers in organic photovoltaics. We have investigated, for the first time, how molecular interactions in the layers effects mechanical properties, including cohesion and the stresses that develop in the bulk heterojunction layer.

Radiation Response of Low Dimensional Carbon Systems

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PROGRAM SCOPE

The objective of this proposal is to discover atomic-scale details governing the ion irradiation response of low dimensional carbon systems, through integrated fundamental experimental and theoretical research. The materials to be studied include graphene, carbon nanotubes (individual or bundled), carbon nanotube films, and their bulk counterparts. Due to their unique geometry and quantum size effects, carbon nanomaterials are expected to have radiation response substantially different from their bulk counterparts. The project will study such differences in each stage of defect development, including damage cascade formation, defect reactions, structural rearrangements, and amorphization. The project will study thermal and electrical carrier transport under the influence of defects for understanding materials degradation issues when used in harsh environments such as outer space and reactors. The project will also explore the possibility of using an ion doping method to purify and tailor nanotubes' properties. The research plan will either utilize or develop a series of novel approaches including (1) using monomer ion and cluster ion irradiation to understand sputtering, stopping, and amorphization mechanisms and their deviation from classical ion-solid interaction theories; (2) using ion irradiation and in situ electrical resistivity measurement on carbon materials (including individual nanotubes to exclude tube-tube interactions) to study distinguishable stages of defect developments; (3) using ion irradiation and in situ transmission electron microscopy to observe dynamic structural evolution; (4) using scanning tunneling microscopy to identify stable defect configurations; and (5) using Raman spectroscopy to study damage buildup, crystalline-to-amorphization transition, and kinetics of defect annealing. The project will integrate experimental studies with atomic scale simulations. Time-dependent density functional theory calculations will be coupled with molecular dynamics simulations to obtain atomic scale details of electron excitation and defect creation. Kinetic Monte Carlo simulations will be developed to predict structural evolution for a large time scale linkable to experiments.

The proposed study will aid in fundamentally understanding the radiation behavior of nanoscale materials. The knowledge will impact a wide range of carbon and non-carbon nanomaterials having a high surface to volume ratio, including nanodots, nanowires and nanomembranes. 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. The project will also have broad societal impact with its educational plans to (1) increase student participation in scientific research, (2) develop curricula, and (3) create e-learning resources to promote public learning. The project will also greatly impact the current progress of building a Center of Ion & Materials Research at the Texas A&M University, which would function as an open ion irradiation user facility for universities, industry, and national laboratories.

Investigating Deformation and Failure Mechanisms in Nanoscale Multilayer Metallic Composites

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PROGRAM SCOPE

The goals of this study by our group at WSU and in collaboration with scientists at LANL are to investigate and discover a new class of nanoscale multilayer metallic (NMM) composites with hybrid coherent/incoherent interfaces (trimetallic system) which possess superior thermo-mechanical properties. The strength of a metallic layered structure depends on many things, including thickness of the layers; we have been investigating how the type of interface between the individual layers plays a large role as well. In thin-film layered structures, it is known that the strength goes up as the layer thickness is decreased. However, the structure of the interface is also important. “Coherent” interfaces, where the crystal structure on both sides is the same, are not as effective at strengthening the materials as “incoherent” interfaces where the crystal structures are different. When the lattice defects that create deformation try to move in these layered structures, the hybrid structure allows a high number to be created but then pins them at the incoherent interface, making the material strong.

FY 2012 HIGHLIGHTS

The results we obtained so far support our hypothesis that a trimetallic NMM composite can be designed which might possess properties exceeding those of the bimetallic systems. Detailed synthesis, measurements, and modeling of deformation on layered structures of coherent (copper/nickel), incoherent (copper/niobium), and hybrid (copper/nickel/niobium) revealed that, for a range of layer thicknesses, the hybrid structure is strongest of all. Furthermore, we have shown that strengthening and thermal stability can be enhanced even more by adding nanoprecipitates within the NNM composites, suggesting that, even within the nanoscale dimension, there are opportunities for further strengthening and hardening using various hardening mechanisms. Moreover, we have extended these discoveries to design core-shell composite nanowires and nanoporous metallic materials. Particularly, we have shown that by adding nanolayers of nickel on ligaments in gold foam can increase the strength of the film by approximately five times. The addition of nickel does not only impact the hardness, but also significantly decreases creep during the indentation process. An atomistic model of core-shell nanowires has been used to explore the differences in the deformation mechanisms with the addition of the plated nickel, and suggests that twinning plays a larger role in a core-shell structure, whereas a similar size structure in a monolithic material is primarily dominated by the nucleation of dislocations. The use of atomistic simulations in conjunction with models of the strengths of foams shows that the predicted performance of the foam using the simulation is within 15% of the experimental data for relatively low density foams. In the next period, we envision to explore combining these concepts for a new class of nanolayer composite metallic-ceramic system for high energy environments.

Radiation Effects in Nanocrystalline Ceramics: Multi-Scale Model and Experiment

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Funding: $220,000

PROGRAM SCOPE

The two main objectives of this project are to (1) discover fundamental phenomena that control interaction of radiation-induced defects with the microstructure of ceramics and (2) determine under what conditions nanocrystalline ceramics exhibit superior radiation resistance as compared to their polycrystalline counterparts. The project is focused on SiC as a model high-temperature ceramic and as a highly promising material for multiple nuclear reactor components (e.g., cladding). Because of the complexity of the defect energy landscape in SiC, understanding fundamental defect properties in this material is challenging. However, the complexity of SiC creates a wealth of possibilities for making exciting scientific discoveries. To meet the aforementioned objectives, we use an integrated approach that includes theory, modeling, and experiments. On a modeling side, we are developing the first radiation model of SiC that is based on first principle properties of defects and that predicts long-term evolution of radiation damage as a function of microstructure and irradiation conditions. On the experimental side, we are carrying out irradiation experiments to determine the effect of grain size reduction on radiation resistance of SiC and to identify other key microstructural features that control this resistance.

FY 2012 HIGHLIGHTS

Three highlights of our research in FY 2012 were chosen for this report. (1) We have investigated small defect clusters in SiC; and we have discovered a “magic” cluster size of 3 carbon interstitials, where the formation energy per interstitial shows a distinct minimum. We proposed this defect to be responsible for the experimentally-observed DII photoluminescence center. The DII center is known to be one of the most persistent defects in SiC, and it is likely to provide a nucleus for growth of larger defect clusters in irradiated SiC. (2) We have investigated the effects of the grain boundary (GB) stress field on the GB sink strength. We have found that while for coarse-grained materials these effects are negligible, GB stresses play a significant role in the kinetics of defect annihilation in fine-grained materials. Contrary to what has been established for larger grain size, in nanomaterials, small-angle GBs are stronger sinks for defects than high-angle GBs and sink strength of some GBs can exceed what is known as the *perfect sink strength*. (3) Our electron irradiation experiments demonstrated that SiC thin films grown by chemical vapour deposition can withstand a higher radiation dose than single crystal SiC before the sample amorphizes. One possible explanation is the presence of a high concentration of stacking faults in these samples. Specifically, our *ab initio* calculations show that key energy barriers to defect recombination in SiC are reduced in the presence of stacking faults which will lead to increased resistance to amorphization.

Using Artificial Microstructures to Understand Microstructure Property Relationship in Metallic Glasses

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Funding:	$110,000

PROGRAM SCOPE

Materials science seeks to correlate microstructure with mechanical properties. Various approaches have been employed to understand this correlation, including conventional direct approaches where the microstructure is varied through processing parameters and composition, and the effects on the mechanical properties determined. Virtual experiments through molecular dynamics simulations have been widely used to investigate structure-property relationships but are limited by today's available computing power, which limits the system size and simulation time. Alternatively, model systems such as colloidal systems have also been employed; however, they exhibit limitations in terms of their predictability and the number of properties that can be varied. Technologically relevant materials have reached a level of complexity that conventional metallurgical strategies as well as above mentioned model and simulation strategies are at their limit.

Therefore, we propose a novel approach to study the microstructure-property relationship—artificial microstructures which allow us to individually and independently vary parameters and thereby determine their individual effects on mechanical properties. The artificial microstructure will be fabricated using our recently developed miniature fabrication method, which allows us to manipulate the material on a length scale ranging from 10 nm to millimeters. Examples of this novel approach are toughening mechanism in metallic glasses, size effects, and the transition from plastic deformation to elastic buckling in metallic glass heterostructures.

FY 2012 HIGHLIGHTS

For metallic glass hexagonal honeycombs, we have revealed three distinct deformation modes as the function of density. At low density, collective buckling is the dominant mechanism; at medium range, there is localized failure and a "shear-band like" progression; and at high densities, shear banding results in global failure. Through this finding, we could identify the optimum density for metallic glass honeycombs in term of toughness.

Tensile ductility in metallic glasses is the main obstacle for broad commercial adaptation of these materials. Using our artificial microstructure approach, we identified microstructural features in metallic glass heterostructures that result in tensile ductility. A structure optimized for tensile ductility should have a spacing of the second phase that is comparable to the critical crack length; this spacing should also coincide with the size of the second phase.

DOE National Laboratories

Nanotwinned Materials for Energy Technologies

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Funding:	$700,000

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 nanoindentor 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 2012 HIGHLIGHTS

Progress was made in 2012 in three main areas: (1) Sputtering has shown that free-standing Ag films can be synthesized with nanotwinned (> 10 nm spacing) fcc grains along with 4H-hexagonal grains (twin-free). We have found that the mechanical properties of the films can be tailored through structural design by controlling the deposition parameters. The free-standing films exhibit high flow stress, on the order of 500 MPa for quasi-static uniaxial tension, and large strain-rate sensitivity. (2) Molecular dynamics simulations of twin-boundary stability show that there are no stable asymmetric twin-boundaries in copper. We evaluated two commonly-used methods to model boundary mobility, finding that one, in which an artificial driving force is used, is unreliable. Finally, a new mechanism of the adsorption of self-interstitials by a twin boundary was simulated, which showed that self-interstitials are arranged as clusters in the twin boundary plane, with atoms in the middle of the cluster having hcp short range order rather fcc. (3) We developed new methodologies for visualizating data acquired through atom probe tomography that enables the interactive rendering of large numbers (> 10 million) of pixel-perfect, lit spheres representing individual atoms (an order of magnitude improvement both in render quality and speed over techniques previously used), which will greatly enhance our ability to quantitatively interpret the data.

Mechanical Behavior of Materials Program

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PROGRAM SCOPE

This program is focused on the development of an understanding of the mechanical behavior of next generation, lightweight, structural materials, in particular involving mechanical properties that are influenced by factors operating at a wide range of length-scales. Our goal is to design, synthesize, and characterize (structurally and mechanically) a new series of hybrid structural materials, whose unique properties derive from hierarchical architectures controlled over length-scales from nano to macro dimensions. The inspiration for these structures is biological; our goal is to defeat the law of mixtures (as in Nature) by devising complex hierarchical structures comprising weak constituents into strong and tough (non-biological) hybrid (polymer-ceramic & metal-ceramic) materials, which display far superior properties to their individual constituents. The research approach combines mechanistic understanding of structural behavior at multiple length-scales, the ability to synthesize such materials using novel techniques, the control of structural features (particularly interfaces) at the nanoscale, the ability to mechanically characterize such structures at atomic, molecular, nano, micro to macroscopic dimensions, and the evaluation of the suitability of these (non-biological) structures/systems for technological application.

FY 2012 HIGHLIGHTS

To date in this program we have developed, processed (using freeze-casting), and fully characterized a suite of Nature-inspired alumina/PMMA and alumina/Al-Si composites, modeled on a “nacre-like” “brick-and-mortar” structure with hard mineral “bricks” separated by a compliant (“lubricant”) polymeric or metallic phase; when optimized, these ceramic materials have unprecedented toughness (>30 MPa√m) but relatively modest strength (~200 MPa). Over the past year, we have concentrated on experimental efforts to define the physics to develop comparable high strength ceramic/polymer and ceramic/metal composites based on the SiC system. The ceramic scaffolds, although far stronger than alumina, tend to be quite brittle, and so we are exploring the use of different compliant phases to understand how to increase their toughness. Additionally, significant efforts have been devoted to theoretical studies to guide our general approach, processing procedures, and design of nano/microstructures in order to increase our fundamental understanding of these new materials. The theoretical modeling effort has been centered on (1) MD-modeling of the freeze-casting process and an homogenized numerical failure model for the hierarchical materials that it produces, and (2) detailed micromechanical modeling for the mechanical properties (modulus, strength, and toughness) of synthetic “brick-and-mortar” structures. In the coming year, we plan to complete our characterization and modeling of SiC scaffolds and to employ high-pressure infiltration of a polymer or preferably a metallic phase to make a suite of higher strength, yet tough, lightweight SiC structural materials.

Evolution of Grain Boundary Networks in Extreme Radiation Environments

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Funding:	$744,000

PROGRAM SCOPE

Advanced nuclear energy systems will require materials to perform for extended periods under conditions of elevated temperatures and extreme radiation. Conventional materials lack the required microstructural stability and will exhibit excessive coarsening, hardening, and swelling. Grain boundaries (GB) in nanocrystalline materials can substantially mitigate this degradation by acting as highly effective sinks for point defects. Unfortunately, nanocrystalline materials can also be unstable with respect to thermal coarsening, so their long-term efficacy requires the microstructure to be stabilized. Our previous work shows that GB networks consisting of a high fraction of annealing twins and related boundaries can be stabilized against thermal coarsening and other interface-mediated degradation.

We are studying whether such GB networks can also enhance microstructural stability under irradiation. The proposed work aims to develop the basic science needed 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 months or years of severe irradiation?* We envision a network in which high free volume, high-energy "random" boundaries act as point defect sinks while the more stable, low energy special boundaries anchor the network, and the entire ensemble is statistically stable over the lifetime of the material. To understand whether this is possible, we will study (1) the coupled evolution of GB structure and point defects, using simulation, theory, and transmission electron microscopy of irradiated materials, and (2) what this implies about the evolution of the GB network, using spatially-resolved diffraction coupled with mesoscale theory and multi-scale simulations.

FY 2012 HIGHLIGHTS

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. These observations are being augmented by 3-D high energy x-ray diffraction microscopy on conventional polycrystalline microstructures that are providing an unprecedented window into the highly coordinated nature of GB networks and how this affects coarsening behavior. These results are also being corroborated through phase field simulations of coarsening behavior. These simulations are being informed by a newly constructed GB energy function that universally treats GB energy anisotropy for all FCC materials.

The various nanostructured materials have also been subjected to electron and proton irradiation to elucidate the mechanisms by which radiation-induced point defects interact with crystallographic defects in the microstructure. An intriguing observation has been of the accumulation (and eventual coalescence) of vacancy loops in the vicinity of coherent Σ3 twin boundaries. This strong correlation is being further investigated in the context of in-situ ion radiation experiments in a TEM.

Deformation Physics of Ultra-Fine-Scale Materials

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Funding:	$964,000

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. The objectives of this program are to study (1) interface-dominated strengthening mechanisms that lead to strengths near the theoretical strength limits in nanolayered materials; (2) the role of interfaces in yield, work hardening, dislocation storage, and recovery; and (3) ductility and fracture mechanisms. 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; characterization of the structure and properties by means of electron microscopy, x-ray diffraction, nanomechanical testing, and electronic transport measurement; and atomistic models of dislocation behavior for the unit processes involved in the deformation of the ultra-fine scale structures. The applicability of the knowledge from this program 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 2012 HIGHLIGHTS

In situ indentation and compression tests in a transmission electron microscope (TEM) were used to measure the shear strength of Cu-Nb interfaces consistent with atomistic calculations. These tests also showed co-deformability of Cu and Nb nanolayers via confined layer slip.

In situ indentation in a TEM revealed co-deformability of ceramic (TiN) nanolayers with metal (Al) at length scales of approximately 5 nm, whereas at layer thickness of 50 nm, plasticity was observed only in the metal layer with cracking in the ceramic. Density functional theory (DFT) calculations revealed a strong dependence of interface shear strength on the chemistry of interfaces: Al/NTi interfaces were stronger in shear than Al/TiN. The effect of interface shear properties on the slip transmission barrier and the co-deformability of the nano-ceramic with nano-metal are being explored.

Multi-Scale Study of the Role of Microstructure in the Deformation Behavior of Hexagonal Material

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Funding:	$981,000

PROGRAM SCOPE

The scope of this program is to use an integrated experimental and theoretical approach to understand the mechanisms of plastic deformation (slip and twin systems) in the HCP metals Zr, Mg, Be. The ultimate aim is to gain a basic understanding that can be applied to improve the forming and usage of these metals for application in the nuclear reactor, automobile, and defense technologies. The complexity of these mechanisms requires a bottom-top approach that links the nanometric-micrometric-milimetric scales for ultimately connecting the slip and twinning mechanisms to the overall mechanical response of polycrystals.

FY 2012 HIGHLIGHTS

We continued with improvements in the development of Crystal Plasticity models for HCP systems and started a new line of research based on developing models for martensitic and twin transformation for application to the novel TWIP and TRIP steels. The work during FY 2012 relied heavily on using neutron and x-ray synchrotron diffraction to investigate evolution of dislocations during plastic deformation, and local stress states in the vicinity of twins. The experimental effort was complemented with Molecular Dynamics and Crystal Plasticity local simulations of twins with the purpose of understanding the local atomic configurations and stress states responsible for the many stages of twinning: nucleation, propagation, growth, and detwinning. To our knowledge, this is the only program in the world that tackles and links all scales of HCP plasticity both at the experimental and the theoretical level. The paradigm applied in our research consists in revealing mechanisms' evolution and interactions at various temperature and strain rate conditions, by testing and simulating complex loading paths.

Electronic and Atomic Response of Ceramic Structures to Irradiation

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Funding:	$1,482,000

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 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 advanced 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 2012 HIGHLIGHTS

Research efforts in FY 2012 have led to advances in understanding the role of energy loss by energetic ions to electrons on irradiation damage production and recovery. A novel large-scale molecular dynamics approach has been developed and applied to investigate the effects of electronic and nuclear energy loss of Au ions, with energies from 0.5 to 100 MeV, on damage production in amorphous silica; the results confirm the experimentally observed synergy of electronic and nuclear energy loss on damage production in amorphous silica. A similar molecular dynamics approach has demonstrated that electronic energy loss by ions can induce defect recovery and epitaxial recrystallization in silicon carbide, confirming experimental observations on recovery in silicon carbide using 20 MeV Pt ions and 870 MeV Pb ions.

Multiscale Mechanical Properties and Alloy Design

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Funding:	$1,220,000

PROGRAM SCOPE

This project seeks fundamental understanding and control of mechanical behavior across multiple length scales. Of special interest are phenomena such as size effects on mechanical properties that cannot be explained by conventional theories. At small scales, our focus is on quantifying the unit events and processes (such as the stresses needed for homogeneous and heterogeneous dislocation nucleation, activation of preexisting dislocations, etc.) that determine the strengths of single crystals. At larger length scales, we are interested in understanding how these fundamental processes interact with microstructural features to produce the observed macroscopic mechanical behavior of polycrystalline metals. Innovative processing techniques and state-of-the-art microanalytical tools are used to synthesize model microstructures and characterize their mechanical behavior. Effects of dislocation core structure, slip systems, and defect states on small-scale mechanical behavior and ductile-brittle transitions are investigated. Theory and simulations, both atomistic and continuum, work closely with the experimental effort and are used to guide and interpret the experiments. The understanding gained from this project will contribute to the development of broad scientific principles for the design of advanced structural materials.

FY 2012 HIGHLIGHTS

Research efforts in FY 2012 have led to significant advances in the detailed understanding of how strength transitions from the theoretical at small scales to the bulk strength at large scales as a function of dislocation density. Tensile tests were performed on as-grown and pre-strained single-crystal Mo-alloy fibers with submicron cross-sections and gage lengths of 9-41 µm. A wide scatter of yield strengths between 1 and 10 GPa was observed for the as-grown fibers. Deformation was dominated by inhomogeneous plastic events, sometimes including Lüders bands. In compression, the behavior is strikingly different with yield strengths showing very little scatter and clustered around the theoretical strength of 10 GPa. In contrast, highly pre-strained fibers exhibited stable plastic flow in tension with significantly lower yield strengths of ~1 GPa and stress-strain behavior very similar to that in compression. A statistical model incorporating the measured dislocation densities was developed to explain the behavior in tension and compression. In parallel, a joint experimental/modeling effort led to significant advances in the detailed understanding of the onset of plastic deformation in single crystals during nanoindentation. Two distinct statistics, one related to thermally activated dislocation nucleation and the other related to the spatial distribution of preexisting dislocations, were combined to develop a unified model. The model describes the observed strong and complex dependence of pop-in probability on indentation direction in NiAl, and indenter radius in Mo, by taking into account effects of stressed volume size, dislocation density, crystallography, and slip anisotropy.

Stability of Nanoclusters in Metal Matrices under Extreme Environments

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Funding:	$958,000

PROGRAM SCOPE

The goals of this project are to understand the formation mechanism, energetics, and fundamental hardening behavior associated with stable nanoclusters in nanostructured metals 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 nanostructured ferritic alloy (NFA), and hence understand their remarkable mechanical properties.

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 2012 HIGHLIGHTS

First-principles theory has been developed to understand the unique material state underlying the stability of Ti-Y-O-enriched nanoclusters in iron. Due to the lattice strain induced by solute atoms, an essential condition for the formation of these nanoclusters is the existence of their exceptionally stable interface. The strain is also important in controlling their size.

Atom probe tomography (APT), scanning transmission electron microscopy (STEM), and in-situ small angle neutron scattering (SANS) experiments have investigated the formation of nanoclusters in mechanically-alloyed 14YWT powder after isothermal annealing. APT and SANS confirmed that nanoclusters form after short-term annealing. STEM imaging indicates that the nanoclusters lack chemical order. Extensive analysis of dislocation structures developed during creep after aging demonstrates ubiquitous interaction with nanoclusters. Near-atomic resolution imaging indicates attractive interaction between nanoclusters and dislocations. A physically-motivated creep model based on a modified Kocks-Argon-Ashby approach has demonstrated excellent agreement with measured creep response.

The distribution of He bubbles in a He-implanted material indicate that ~48.6% of the He bubbles are located on nanoclusters, ~4.4% on precipitates, ~14.4% on grain boundaries, ~12.2% on dislocations, and the remainder as isolated bubbles in the ferrite. These TEM and APT results support the hypothesis that the nanoclusters trap He and thereby reduce the susceptibility to He embrittlement during neutron irradiation. STEM methods have been developed for imaging dislocation-helium bubble interactions to enable quantification of the distribution of the He bubbles between the microstructural features present in nanoindented and He implanted 14YWT NFA specimens.

Crack Tip Mechanisms Driving Environmental Degradation

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Funding:	$651,000

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. Oxidation at liquid-solid, gas-solid and solid-solid interfaces will be evaluated to establish basic processes leading to grain boundary degradation. Our research builds on recent analytical transmission electron microscopy (ATEM) measurements revealing unexpected nanometer-scale crack opening and oxidation reactions driving intergranular (IG) cracking of LWR structural alloys in service. ATEM measurements have also shown dramatic compositional changes and nanoporosity at the metal grain boundary leading the crack tip. Kinetic development of such features can only be explained by oxidation-induced vacancy injection. Collective evidence and analyses have suggested that IG penetrative degradation can advance in many corrosion-resistant alloys by selective grain-boundary oxidation even at low temperatures. Direct mechanistic links have been made among degradation of corrosion-resistant structural alloys in water, supercritical-water and high-temperature gaseous environments. These measurements and observations are generally inconsistent with continuum mechanics and electrochemical models of environmental degradation and point toward the need for atomic and molecular level understanding of the processes.

FY 2012 HIGHLIGHTS

Unexpected solid-state internal oxidation or sulfidation has been discovered in nickel-chromium alloys during exposure in hydrogenated, high temperature water environments using high-resolution analytical electron microscopy and atom probe tomography. Selective oxidation of chromium was found to drive penetrative degradation along dislocations at crack walls and surfaces, preventing formation of a protective oxide layer in high-chromium, nickel alloys. Unexpected internal sulfidation was identified leading grain boundary oxidation during localized corrosion of lower chromium, nickel alloys. Selective oxidation experiments were also performed isolating effects of chromium, iron, aluminum and silicon additions on intergranular corrosion and cracking in binary nickel alloys. In situ, transmission electron microscopy oxidation studies were completed on nickel and nickel-chromium alloy nanoparticles to establish reaction rates and investigate vacancy injection during oxidation. Finally, basic modeling of oxidation processes continued and a single analytical framework was created to resolve the mechanistic gap between oxide growth rates for thin and thick films. This model is now being adapted to more complex slip oxidation issues.

Nanomechanics and Nanometallurgy of Boundaries

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Funding:	$736,000

PROGRAM SCOPE

This project builds off of recent success in understanding mechanically-driven abnormal grain growth in nanostructured alloys. Through this program, we have uncovered behaviors in nanostructured metals that seem to contradict basic tenants of metallurgy. Specifically, while the driving force for mechanically-induced grain growth is understood to be associated with elastic and plastic strain energy minimization, the exceedingly low mobility of metal grain boundaries at low homologous temperatures ($T<<0.3T_{mp}$) was previously thought to be insurmountable. New concepts of detwinning and dislocation-analogue boundary motion help to explain this diffusionless or diffusion-limited behavior. We have come to realize that in the absence of traditional dislocation plasticity, the well-known grain boundary sliding process for tangential motion of the grain boundaries is complimented by perpendicular motion of the grain boundary resulting in grain growth. In the coming three years, the goal of the program is to take advantage of this new class of boundary-mediated deformation processes as a means to dissipate energy. Nanostructured alloys are well known for their exceptional strength, but they often suffer from limited ductility, a classic materials paradox. A few exceptions from our own work and from the literature suggest that there is a pathway to enable both enhanced strength and improved ductility. Our core hypothesis for this program is that the ductility, toughness, and flaw tolerance of nanostructured alloys can be dramatically enhanced by enabling mechanically-induced boundary motion. To explore this hypothesis, our project will continue to rely on an ICME-inspired balance of computational modeling and experimentation at multiple length scales from the atomistic to the macroscale.

FY 2012 HIGHLIGHTS

Our new cryoindenter has revealed rapid indentation-induced grain growth in nanotwinned high purity Cu at both 77K and 4K, at temperatures where diffusional processes are extraordinarily slow. Precession TEM diffraction reveals evidence of both detwinning and prevalence of $\Sigma 7$ grain boundaries (*Scripta Materialia* paper accepted pending minor revisions). Molecular dynamics simulations suggest that two mechanisms may be in play: both detwinning and dislocation channeling along the twin boundary. Also, simulations reveal that Σ7 boundaries possess exceptionally high mobility and their mobility is surprisingly anti-thermal—increasing with decreasing temperature.

Neutron Scattering

Institutions Receiving Grants

In-situ Neutron Scattering Determination of 3D Phase-Morphology Correlations in Fullerene Block Copolymer Systems

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Funding:	$319,000

PROGRAM SCOPE

The efficiencies of organic photovoltaic (OPV) materials and devices must be enhanced several fold to make these next generation solar cells competitive with current inorganic or hybrid photovoltaics systems. To this end, the majority of current research in OPVs is largely focused on creating or developing new materials, processes, and constructs for more efficient devices, which for the most part ignores a fundamental understanding of morphology and processing effects. In order to achieve profound advances in OPVs, a fundamental understanding of a correlation between structure, morphology, processing, and efficiency is however essential. The research objectives of this project have focused on investigating model disordered bulk heterojunction (BHJ) systems consisting of mixtures of functionalized fullerenes and conjugated homopolymers, as well as model ordered-BHJs that involve block copolymers (BCPs) as nanostructured templates for ordered BHJ fabrication with electron accepting nanoparticles. The tunability of the morphology and structure of these model systems through synthesis of new materials, novel processing strategies, and characterization, of which a large component is neutron and x-ray scattering, allows us to test fundamental issues that are currently poorly understood, and will ultimately offer potential for dramatic improvements in OPVs. Fundamental questions that we aim to address include the following: (1) *How does the phase domain architecture, i.e., morphology of BHJ blend (phase domain evolution and crystallinity of both conjugated polymer and nanoparticle), correlate with OPV efficiency?* (2) *How do the electronic levels of fullerene derivatives in BHJ blends impact the evolving morphology and efficiency?* (3) *Can we control the Z-segregated profile in BHJ blends using soft surface energy confinement?* (4) *Can fullerene percolation in selective BCP domains be attained?* (5) *How can simulations help understand these issues at a fundamental level?*

FY 2012 HIGHLIGHTS

We have developed direct correlations between neutron scattering established morphology in device geometry with its solar cell performance and processing temperature conditions for a cross-homologous series of 9 conjugated polymer and electron-accepting nanoparticles combinations. These relationships establish fundamental relations between the complex hierarchical architecture of disordered BHJs with the corresponding photoelectronic device efficiency and the complex molecular fullerene-conjugated polymer interactions for the synthesized and commercial nanoparticles. Advanced rotational small angle neutron scattering, neutron reflectivity, grazing incidence x-ray scattering, and optical imaging techniques, coupled with hybrid self-consistent field simulations, determine the detailed hierarchical structural information of these model fullerene-BCP systems to address the critical questions (1-5) listed above in both disordered and ordered BHJs.

Vibrational Entropy Studies using Inelastic Neutron Scattering

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Students:	0 Postdoctoral Fellow(s), 3 Graduate(s), 0 Undergraduate(s)
Funding:	$190,000

PROGRAM SCOPE

The objective is to understand the origin of vibrational entropy and how it affects phase stability and phase transformations in metals and oxides. The work addresses cases where vibrational entropy is likely to be both large and interesting, especially at high temperatures where there can be significant effects from phonon-phonon interactions and electron-phonon interactions.

Our experimental effort relies on inelastic neutron scattering performed at national user facilities, such as the Spallation Neutron Source and ORNL, and nuclear resonant inelastic x-ray scattering measurements at the Advanced Photon Source, ANL. Analysis of the experimental data gives vibrational spectra of the materials, i.e., their phonon densities of states (DOS), from which we obtain the vibrational entropies of different materials. At high temperatures, there is a hierarchy of anharmonic effects; we have developed methods for separating them into quasiharmonic entropy and anharmonic entropy from cubic and quartic behavior of different orders. Last year, we found an important connection between negative thermal expansion and quartic anharmonicity that motivates new studies on oxides, silicates, and intermetallic compounds.

FY 2012 HIGHLIGHTS

We published results showing strong anharmonicities in the rutile oxides TiO_2 and SnO_2 at elevated temperatures. The measurements used Raman spectroscopy, and the method of data analysis was uniquely rigorous. In a second piece of research, we showed how electronic changes around Fe atom impurities alter the vibrational dynamics and entropy of fcc Au.

Neutron and X-Ray Studies of Spin and Charge Manipulation in Magnetic Nanostructures

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PROGRAM SCOPE

The interrogation and manipulation of electron charge, spin, and magnetization in thin films and magnetic nanostructures is currently one of the frontier areas of research in condensed matter physics and materials science. These include issues that are directly related to scaling down the dimensions such that finite size, interfacial, and collective effects dominate the behavior. Magnetic materials and devices have also played a major role in magnetic information technologies. We are carrying out a research program to study both the static and dynamical properties of these magnetic systems. The main investigative tools we use are the techniques of neutron and x-ray scattering carried out at the national synchrotron x-ray and neutron facilities combined with extensive in-house characterization facilities for structural, magnetic, transport, and imaging measurements.

FY 2012 HIGHLIGHTS

Over the past period, we have discovered and explored a number of new phenomena which present exciting possibilities for further research. Some of these findings that provide the impetus for new research directions include: showing that domain fluctuations (which give rise to noise in magnetic circuits) in antiferromagnets exhibit jamming behavior with similar universal characteristics seen in totally different systems such as granular media or colloidal gels, demonstrating the first reconstructed image of magnetic domain structures using diffraction imaging with coherent x-ray beams, uncovering new memories and hidden rotational symmetries in magnetic domains using x-ray speckle patterns, seeing novel non-equilibrium effects at phase transitions in magnetic films driven by a laser pulse, and preliminary results of very interesting “electronic and magnetic reconstruction” effects at ferromagnetic oxide interfaces driven by electric fields or juxtaposition to non-magnetic oxides.

The research planned for the next funding cycle will build on previous research results and will focus on two areas. The first area is time-dependent studies of magnetic nanostructures. This research will probe the physics of magnetic nanostructures by studying the underlying excitations of the system with atomic depth resolution and nm lateral resolution. The time scales will cover the range from seconds to femtoseconds, using a variety of techniques and will probe phenomena ranging from slow magnetic domain wall fluctuations to ultrafast magnetization dynamics. The second area is interfacial phenomena in oxides. We will study the fundamental interfacial phenomena in complex oxide interfaces. This will include understanding the role of electric field effects in piezoelectric-ferromagnetic heterostructures and probing electronic reconstruction that occurs at oxide interfaces.

Novel Molecular Materials for Hydrogen Storage Applications

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Funding:	$334,000

PROGRAM SCOPE

The goal of this project is to use high pressure to synthesize new materials for hydrogen storage. The project is also directed at exploring pressure-induced interactions of hydrides, borohydrides, and boranes with H_2 and D_2 in an effort to increase the hydrogen content and re-hydrogenate spent fuel.

We will be using pressures ranging from a few bars to hundreds of kilobars to investigate a range of molecular materials as well as hydrogen-rich materials. Using national facilities such as APS, NSLS, and SNS, we will study the fundamental interactions between H_2 and the host materials in detail. These studies involving Raman and infrared spectroscopies and x-ray and neutron diffraction will help us understand how pressure modifies chemical interactions. These studies will form the input to theoretical calculations that will in turn be used to design pathways to lowering the synthesis pressures and also alternate synthesis routes.

While molecular compounds of H_2 are stabilized by weak chemical forces induced by pressure, many of these compounds which are expected to remain in a pressure-induced, metastable chemical equilibrium can indeed be quenched to ambient pressures at low temperatures. We will also be exploring alternate strategies to encapsulate such compounds either mechanically or chemically so that we can raise their stability temperature thereby making them available for potential application as fuel.

FY 2012 HIGHLIGHTS

In the Xe-H_2 system, we had earlier discovered the compound $Xe(H_2)_7$ that is found to be stable at phenomenally high pressures. While there are several intriguing questions that need to be answered here, we focused on the low pressure region (60 kbars). We developed better single crystal analysis techniques to harness structural information from the data obtained at APS. The lowest pressure phase was identified to be $Xe(H_2)_{24}$ making this the compound with the highest hydrogen stoichiometry known. Detailed high pressure-low temperature diffraction studies done at the synchrotron beamline 16 ID-B of APS (HPCAT) have shown that we can indeed retain this phase at ambient pressure and at temperatures as high as 90 K which is above liquid nitrogen temperatures.

We have also characterized the structure of the new H_2O-H_2 clathrate phase synthesized at low pressures and low temperatures. We have investigated the interaction of H_2 with two frustrated Lewis pair complexes—Me_2NHBH_3 and $N_2B_2H_4Me_4$—in an effort to elucidate the detailed thermochemistry and possibility of building alternate avenues to hydrogenation of ammonia borane.

From Interfaces to Bulk: Effects of the Interfacial Regions on Ionic Polymers, Experimental-Computational Studies

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Funding:	$182,000

PROGRAM SCOPE

The necessity for responsive multifunctional materials manifests itself in a large number of applications—from clean energy generation and storage to self-healing layers and drug delivery media—all in the core of the national needs. 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. The proposed research investigates the factors that control the interfacial regions within ionic polymers on multiple length scales.

To attain this goal, a conjunction of experimental and computational studies has been carried out on a series of polymers whose chemical architecture will be 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 (7% random). 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 0.1 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 will be 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 and similar systems to those studied experimentally will provide molecular understanding of the structure and dynamics and explore length and time scales that cannot be probed by the experimental tools.

FY 2012 HIGHLIGHTS

Small angle neutron studies have identified spherical micelles with the block that provides mechanical stability partially mixed with the ionic group in hydrophobic solvents. Further insight into the migration of water was obtained from neutron reflectometry.

Computationally, we have fully characterized a single penta-block in solution. We have prepared atomistically membranes and initiated the first step of coarse graining the pentablock co-polymers.

Neutron and X-Ray Scattering Investigation of Electron-Phonon Effects in Cuprate Superconductors and Related Compounds

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Funding: $150,000

PROGRAM SCOPE

The goal of the program is to use neutron and x-ray scattering to uncover fundamental mechanisms behind high temperature superconductivity, stripe physics, and electrochromism. These phenomena originate from complex electronic correlations and unconventional electron-phonon coupling, and there are strong indications that they share some underlying physics. The particular focus of the program is on the interactions of electrons with the atomic lattice as well as on dynamic charge stripes. The systems that were investigated were Fe-based superconductors, copper oxide superconductors, and stripe-ordered nickel oxides. Our previous work on Fe-based superconductors demonstrated that the interactions between the electron charge and the atomic lattice is not very important, but the interaction between the electronic and magnetic moments might be. Thus, we concentrated on spin-phonon coupling investigations. In copper oxide superconductors, we continued to make progress in understanding the nature of strong phonon anomalies that were reported previously by our group and others. In particular, we focused on trying to distinguish between the interactions of phonons with electronic quasiparticles from the interactions with collective modes as well as the origin of superconductivity. This research direction required us to perform angle-resolved photoemission (ARPES) measurements to complement the neutron/x-ray studies as well as to look into collective electronic charge excitations associated with stripe physics. We are in the beginning phase of the investigation of dynamic charge stripes. We are doing a lot of measurements on a model stripe system, $La_{2-x}Sr_xNiO_4$, and obtained beamitme on a new spectrometer at the SNS, HYSPEC, to look at a stripe-ordered cuprate during the next fiscal year.

FY 2012 HIGHLIGHTS

Using inelastic neutron scattering on $Fe_{1.08}Te$, we found incommensurate magnetic fluctuations above the Neel temperature, even though the ordered state is bicollinear and commensurate with gapped spin waves. We showed that this behavior results from a lock-in transition accompanied by an atomic lattice distortion caused by magnetic anisotropy. Our finding solved one of the most significant puzzles in the field. Our ARPES experiments on overdoped $La_{2-x}Sr_xCuO_4$ showed that giant phonon anomaly that was previously reported is a result of an interaction of bond-stretching phonons with a collective mode, not with conduction electrons, resolving an important question in the field of the high T_c cuprates. We also found and characterized dynamic charge stripe spectrum in $La_{1.67}Sr_{0.33}NiO_4$, which has never been observed before by a direct probe such as inelastic neutron scattering.

Neutron Scattering Studies of Classical and Quantum Fluids in Nanoporous Media

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Funding:	$150,000

PROGRAM SCOPE

We are performing world-class neutron scattering measurements of the atomic momentum distribution, n(k); Bose-Einstein condensation (BEC); and the collective modes of quantum liquids and solids. Both BEC and low-energy collective modes, such as the phonon-roton mode of liquid 4He, are uniquely measured using neutrons. Since superflow and superconductivity arise from BEC, data on BEC and modes bring critically important information to superflow and related thermodynamic properties. The measurements are carried out on the ARCS instrument at the Spallation Neutron Source (SNS) and on IN5 and IN6 at the Institut Laue Langevin (ILL), France. Following survey measurements of BEC and n(k) in liquid 4He under pressure in 2010 and 2011, we measured the temperature dependence of BEC and n(k) at 24 bar (near solidification) with new precision on ARCS at SNS. Near solidification, the condensate fraction in the liquid is small (3%). We find also that BEC is coupled to n(k); the onset of BEC is accompanied by a narrowing of the atomic momentum distribution, n(k) for $k > 0$. This new finding is of intrinsic interest for superflow in strongly interacting systems. Measurements of the phonon-roton and layer modes of liquid 4He confined in porous media have been made at ILL. The goal is to reveal the impact of nanoscale disorder on BEC, modes, and superflow. These measurements show that BEC can be localized to patches or islands by disorder. In a third project, we are developing methods to extract the intrinsic motional mean square displacements (MSD) of hydrogen in proteins, both from measurements and from simulations. The MSD is widely measured using neutrons and is used as an indicator of protein function. The simulations are done in collaboration with the Center for Molecular Biology at UT-ORNL using supercomputers.

FY 2012 HIGHLIGHTS

We have observed that the onset of BEC, the condensation of a measurable fraction of the Bosons into the zero momentum ($k = 0$) state, is associated with a narrowing of the atomic momentum distribution, n(k), over the higher $k > 0$ states. There is a coupling between occupation of the $k =0$ and $k > 0$ states not previously observed. We have also shown unambiguously that well-defined phonon-roton modes exist at temperatures above the superfluid phase in liquid 4He in porous media. Well–defined modes exist where there is BEC. In disorder (in porous media) at temperatures above the superfluid phase, BEC exists but is is localized to patches. We have determined the density of states of amorphous solid helium for the first time, showing that it is very similar to that in polycrystalline solid helium.

Development of New Methods to Study Materials Structure using Spin Echo Scattering Angle Measurement (SESAME) of Neutrons

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Funding:	$248,000

PROGRAM SCOPE

Spin Echo Scattering Angle Measurement (SESAME) is a technique for high-resolution neutron diffraction that encodes information about the neutron scattering angle into the neutron polarization. The technique does not require highly monochromatic neutrons and dispenses with slits and collimators, so it can use neutrons more effectively than traditional methods, preserving signal intensity while achieving very high resolution.

In this project, we will construct an optimized system that will permit SESAME to measure density correlations over distances from 20 nm to about 3000 nm using neutrons in a wavelength band from 0.3 nm to 1 nm. This equipment, which will be tested using neutrons from the Low Energy Neutron Source (LENS) at Indiana University, will be suitable for installation on polarized neutron spectrometers at major neutron sources. We will use the SESAME technique to carry out a number of scientific investigations where the structural information provided by SESAME will complement that from other techniques and potentially provide new scientific insights. Systems we intend to study include mixtures of colloids and polymers that are relevant to many industrial products such as food, cosmetics and structural materials; colloidal fluids confined in grooves or pores which are relevant both to biological processes, such as blood flow, as well as to new techniques involving microfluidics; and the dewetting of polymers from surfaces which relate to both coating and lubrication technologies.

FY 2012 HIGHLIGHTS

Working with Professor Mike Snow and his team at Indiana University, we have implemented at LENS the first ever SESAME instrument to use polarized ^{3}He as a polarization analyzer and we have made test measurements on a known system of colloidal silica to demonstrate its performance.

Using our own equipment installed on the Asterix reflectometer at LANSCE, we have measured colloidal dispersions of poly(methylmethacrylate) (PMMA) spheres dispersed in decalin with small amounts of added polystyrene of different molecular weight. We have found that SESAME provides a sensitive method to measure both long- and short-range correlations. Our measurements demonstrate the formation of small clusters under the influence of polymer depletants and the eventual assembly of these clusters into larger aggregates. The unique capability of SESAME to measure accurately and rapidly the total coherent neutron scattering cross section allows us to monitor these transitions in real time.

Using the SESAME instrument at the ISIS facility in the UK, we have explored the behavior of a colloidal dispersion of silica when it is placed next to a silicon chip with multiple, parallel, rectangular channels. The colloidal particles move preferentially into the channels and appear to form close packed layers.

This counter-intuitive result supports the conclusion of recent measurements made using synchrotron x-rays at the PSI in Switzerland.

Polarized ^{3}He Neutron Spin Filters

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Funding:	$310,000

PROGRAM SCOPE

The goal of this grant to Indiana University and subcontractors at Hamilton College and Wisconsin and the associated Interagency Agreement with NIST is to extend the technique of polarized neutron scattering by the development and application of polarized ^{3}He-based neutron spin filters. The long-term support from the Office of Science for this work has led to the establishment of ^{3}He neutron spin filters as a user option on neutron scattering spectrometers at NIST and established the foundation for their use on several spectrometers at SNS.

FY 2012 HIGHLIGHTS

One of the main goals of the Indiana University proposed research is to conduct neutron spin echo measurements on the SESAME spectrometer at the LENS neutron source at IU in collaboration with the group of Roger Pynn. Our polarized ^{3}He system was ready and tested in May 2012 with a ^{3}He polarization estimated in off-line tests from EPR measurements of 75%. SESAME observed spin echo at LENS in June 2012 and installed a new 2D position sensitive ^{3}He detector for quantitative measurements in late August 2012 just before the September and October 2012 LENS run cycles. We conducted a series of measurements to characterize the interference contrast of the SESAME spin echo instrument as a function of the beam size. The flat-windowed, 6 cm diameter polarized ^{3}He analyzer provided by NIST allowed us to perform this exploration. From the data, it is clear that we will be able to use beams as large as 2.5 cm x 2.5 cm for SESAME spin echo measurements.

We also conducted a first measurement of the one-dimensional projection of the pair correlation function (the Patterson function G(z)) for a sample of anodic aluminum which has been measured previously on ASTERIX. The agreement is good for small correlation lengths z but there is a discrepancy in the intensity of the peak near 100 nm. We are investigating whether this discrepancy might be due to the narrower phase space acceptance of the supermirror-based polarization analyzer on ASTERIX. If so, it would indicate an advantage for the use of polarized ^{3}He with SESAME. We will investigate this question soon in a measurement at ASTERIX.

Institute for Quantum Matter at Johns Hopkins University

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Funding:	$1,300,000

PROGRAM SCOPE

The Institute for Quantum Matter (IQM) mission is to realize, characterize, understand, and control novel quantum correlated states of matter. Progress cannot be achieved with narrow expertise but occurs when dedicated scientists with common interests and complementary expertise cooperate. We therefore assembled within IQM expertise in the pertinent areas of spectroscopy, synthesis, and theory. The corresponding PIs are Broholm and Armitage for neutron and photon spectroscopy, Cava and McQueen spanning synthesis of quantum magnets and superconductors, and Tchernyshyov and Tesanovic (first half of 2012) covering the theory of magnetism and superconductivity. IQM is involved at the forefront of the development of methods to elucidate the structure and dynamical properties of materials through neutron scattering and THz optical techniques.

FY 2012 HIGHLIGHTS

The IQM provided experimental evidence for and theory of novel quantum correlated states of matter. In the area of magnetism, several materials were discovered with unusual properties that relate to theoretically predicted anomalous forms of magnetism. For example, an essentially quantum mechanical form of valence bond magnetism was discovered in $LiZn_3Mo_3O_8$. We discovered extremely short-range magnetic correlations in $Pr_2Zr_2O_7$ characterized by a divergence free configuration much as in the flow of water. The excitations were shown to be magnetically monopolar with quantum dynamics. A strongly disordered form of quantum magnetism was characterized in $Ba_3CuSb_2O_9$. A new honeycomb antiferromagnetic was discovered (Cu_5SbO_6) and characterized through bulk measurements. Theoretical proposals were made to probe anomalous magnetic excitations in quantum spin ice and in quantum spin liquids.

In the area of superconductivity, we detected Friedel-like oscillations from interstitial iron in an Iron chalcogenide superconductor $Fe_{1+y}Te_{1-x}Se_x$. It was shown that the magnetic Friedel oscillations extend into the superconducting volume. The data were shown to be consistent with the prevailing band theory of the iron plane when subjected to the effects of an interstitial local moment. THz spectroscopy provided direct evidence for charge dynamics fluctuations in the under-doped superconducting state of $La_{2-x}Sr_xCuO_4$.

Finally, the THz response and colossal Kerr rotation was detected from the surface state of the topological insulator Bi_2Se_3. The results have been published in prominent journals, including *Physical Review Letters*, *Science*, *Nature*, and *Nature Materials*.

A Unified Effort for Crystal Growth, Neutron Scattering, and X-Ray Scattering Studies of Novel Correlated Electron Materials

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Funding:	$288,000

PROGRAM SCOPE

Our research activities are focused on understanding the fundamental science of complex electronic and magnetic materials. Much of the research involves performing neutron and x-ray scattering experiments on single crystal samples to investigate the spin, charge, lattice, and orbital correlations which are central to the exotic physics in these systems. We have also performed thermodynamic and transport measurements to provide a comprehensive picture of the microscopic behavior. Growing single crystal samples is a crucial aspect of this research, as this allows one to obtain the highest quality data to make precise tests of the leading theoretical ideas.

The idea that the doped copper-oxides may be on the verge of quantum disorder has led to great interest in the possibility of quantum disordered spin ground states (called the spin liquid). It is expected that such systems will have remarkable new properties, such as the fractionalization of the spin quantum number. For example, the usual S=1 spin wave excitation may be broken up into a pair of S=1/2 excitations (called spinons). This phenomenon is well known in one-dimensional spin chains, but has so far been elusive in two-dimensional systems. Spin liquids are believed to play an important role in theories for the high-transition-temperature superconductors, and they have been proposed in applications in quantum information. A major thrust of our research is to try and realize quantum spin liquid ground states in kagome lattice systems which are composed of corner-sharing triangles. The lattices that comprise these materials are known to frustrate classical magnetic ordering. By studying the family of S=1/2 kagomé lattice systems $Zn_xCu_{3-x}(OH)_6Cl_2$ and $Mg_xCu_{3-x}(OH)_6Cl_2$, we hope to define the physics of these novel quantum states. Another major thrust is to better understand the broken symmetries which characterize the electronic states of the copper-oxide superconductors, using bulk scattering experiments.

FY 2012 HIGHLIGHTS

We have succeeded in performing a set of neutron scattering measurements on large single crystals of ideal S=1/2 kagome lattice materials. The main result is that we have observed evidence for fractionalized excitations in the form of a continuum of scattering—this is a remarkable first in a two-dimensional quantum magnet. In addition, we have determined that the spin-spin correlation length is of short-range, yet no spin-gap is observed (in contrast to expectations from theory). This latter observation may be related to additional terms in the spin Hamiltonian, which we have also characterized by measurements of the magnetic susceptibility on our single crystal samples.

Neutron and X-Ray Scattering Studies of the Liquid-Liquid Transition in Supercooled Confined Water and the Phonon-Like Collective Excitations in Globular Proteins

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Funding:	$350,000

PROGRAM SCOPE

We are extensively studying the thermodynamics and dynamics of supercooled confined water in pressure-temperature phase space using elastic, quasi-elastic (QENS), and inelastic (INS) neutron scattering techniques. By confining water in nano-porous silica material MCM-41-S, we can suppress the temperature of the homogenous nucleation of the confined water down to at least 130K. This method allows us to study the anomalous properties of deeply supercooled water in the so-called “no-man’s land” range of temperatures. We did a series of measurements of the density of water as a function of T along various isobars (i.e., determined the equation of state of the confined water). This allowed us to show the plausibility of a first order liquid-liquid transition line at higher pressures. We observed a fragile-to-strong dynamic crossover at T_L=225K at lower pressures, which allowed us to map out the Widom line (the extension of the liquid-liquid phase transition line into the one phase region). We are now applying similar methods to map out the entire locus of the Widom line in order to locate its endpoint, which is the liquid-liquid critical point.

We continue to explore the dynamics of hydration water in aged white cement pastes as a function of temperature (especially at low temperatures) and establish the connection between its observed crossover temperature and the mechanical strength of the cement at low temperatures. Additives such as super-plasticizers are able to confer high plasticity and flowability to cement pastes. We therefore are making an extensive QENS investigation of the translational dynamics of hydration water in such cement pastes with additives in order to elucidate the microscopic origin of these conferred functional properties.

We are studying the intra-protein phonon-like excitations and their damping in globular proteins. Our objective is to establish relations between the phonon-like collective motions in these proteins and their biological functions.

FY 2012 HIGHLIGHTS

We have made librational and translational density of state measurements of water confined in MCM-41 nanoporous silica material at supercooled temperatures using INS spectroscopy and have shown the existence of the first-order transition line between high-density and low-density liquid water, which is the thermodynamic extension of the corresponding line between high-density and low-density amorphous ice. We have determined the microstructure of calcium silicate hydrate, the primary binding phase of Ordinary Portland Cement, using small-angle neutron scattering. We have observed a softening of specific intra-protein phonons above the minimum hydration level required for enzymatic function in hydrated lysozyme powders using inelastic x-ray scattering spectroscopy.

Thermodynamics of Self-Assembly in Globular Protein-Polymer Conjugates

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Funding:	$250,000

PROGRAM SCOPE

Harnessing globular proteins and enzymes in materials can potentially enable Nature's machinery for energy conversion and utilization to be exploited in the design of novel bioelectronics and biocatalysts for applications such as solar energy conversion, carbon dioxide reduction and sequestration, or hydrogen production. The self-assembly of block copolymers containing an enzyme or optically-active protein block could provide 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 biofunctional nanomaterials.

Both the folded protein chain shape and the specific interactions between globular proteins differ significantly from traditional Gaussian coil block copolymers, adding 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 hybrjds; and we aim to answer three fundamental scientific questions. (1) *What is the effect of protein shape (steric interactions) on self-assembly?* (2) *What is the effect of protein-protein interactions on self-assembly*? (3) *How do the processing conditions used to induce self-assembly affect the folded structure and function of the globular protein block in a block copolymer?*

FY 2012 HIGHLIGHTS

Processing methods to induce nanostructure formation were explored in detail, demonstrating that the structure of the block copolymers in solution is critical to the type of nanostructure formed. When self-assembly is performed in a nonselective solvent, block copolymer-like structures, such as hexagonal cylinders, perforated lamellae, and lamellae, are formed. However, when the materials are self-assembled from protein-selective solvents where the polymer has a tendency to aggregate as demonstrated by small-angle neutron scattering (SANS), disordered micellar phases are formed. It was also demonstrated that nonselective solvents are able to preserve a high fraction of protein function in the solid state. Further work mapped these detailed structure transitions, identifying both order-order transitions and order-disorder transitions as a function of temperature and concentration in the materials. SANS experiments demonstrate that temperature-dependent order-order transitions in the materials are driven by the redistribution of water within the protein and polymer nanodomains. Trends in phase behavior with changing the polymer fraction in the protein-polymer block copolymers suggest that solvent-mediated protein-polymer repulsive interactions are critical to the self-assembly process.

Crystal Growth and Scattering Studies of Model Cuprate Superconductors

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Funding:	$290,000

PROGRAM SCOPE

The goal this effort will be the investigation of the $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ compounds, arguably the most desirable unconventional superconductors due to their record values of T_c and their relatively simple crystal structures. The PI's group is the only one in the world to have mastered the growth of sizable single crystals of the simplest ($n = 1$) member of this materials family, $HgBa_2CuO_{4+\delta}$ (Hg1201). The proposed work will build on the PI's observation (*Nature,* 2008), using neutron scattering, of an unusual q=0 magnetic order in the pseudogap phase of Hg1201. It will furthermore build on the subsequent discovery of novel magnetic excitations associated with this order (*Nature,* 2010). These findings are important, since they support the distinct theoretical proposal that the phase diagram is controlled by an underlying quantum critical point, and because it is thought by many that magnetic fluctuations play an important role in bringing about the superconductivity. These initial neutron scattering results for Hg1201, which were made possible by prior DOE support, will be extended over a wide range in parameter space (energy, momentum, temperature, hole concentration) and complemented by transport, torque, and x-ray measurements. 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 have a far-reaching impact beyond the PI's own scattering experiments through collaborations with experts using complementary experimental tools. The hope is to conclusively identify the minimal model required for a proper theoretical description of the enigmatic cuprates.

FY 2012 HIGHLIGHTS

Our inelastic neutron scattering work revealed a second novel excitation in the pseudogap state in both optimally-doped (T_c=95 K) and moderately underdoped (T_c= 65 K) Hg1201 (*Nature Physics,* 2012). These excitations are nearly dispersionless, centered at the zone center (q=0), exist throughout the entire Brillouin zone, and exhibit an interesting correlation with conventional (antiferomagnetic) excitations. Torque magnetization measurements have been completed, indicating that superconducting fluctuations in Hg1201 extend over a relatively narrow temperature range and decay in an unusual exponential fashion (*preprint*). Planar resistivity measurements have been completed that demonstrate Fermi-liquid-like properties deep in the pseudogap phase and allowed the determination of the universal resistance per copper-oxygen sheet (*preprint*). Collaborative optical conductivity measurements confirm the Fermi-liquid-like transport behavior (*preprint*). Synchrotron x-ray measurements confirmed the prior discovery of oxygen-chain order near optimal doping. Initial synthesis of Hg1212 has yielded small crystals. Last, but not least, new collaborations have been initiated (e.g., resonant ultrasound, Kerr effect).

Neutron Scattering Studies of Cobaltite Crystals and Heterostructures

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Funding:	$150,000

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 inter-disciplinary 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 2012 HIGHLIGHTS

One of the aspects of this research that has very quickly yielded significant breakthroughs is the understanding we have obtained of oxygen defect ordering in very thin epitaxial films. We have uncovered a deep interplay between the mechanical strain state of these films and their propensity for oxygen vacancy formation and ordering, which is found to have a large impact on magnetic and electronic properties near interfaces. In addition to providing a means to mitigate, or perhaps even eliminate, well-known problems with interfacial magnetism and transport in these materials (which is germane to the development of oxide electronics), this also opens up the possibility of precisely controlling oxygen transport, vital to oxide fuel cells and gas separation membranes for example.

Optics for Advanced Neutron Imaging and Scattering

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PROGRAM SCOPE

We are developing novel neutron focusing optics, which can be used to enhance the performance of existing neutron scattering instruments, to improve the resolution of neutron imaging techniques and, hence, to enable new science. We have demonstrated the focusing capabilities of grazing incidence neutron imaging mirrors based on full figures of revolution. The technique used to produce the mirrors is the electroformed nickel replication (ENR) process, which we have been developing at Marshall Space Flight Center for hard-x-ray astronomy. In this technique, pure nickel or nickel-alloy mirror shells are electroformed onto a figured and superpolished nickel-plated aluminum cylindrical mandrel from which they are later released by differential thermal contraction. The resulting full shell mirrors can be nested to increase neutron throughput. We are adapting the mirror fabrication ENR technology for neutron applications and developing the neutron replicated multilayer technology to improve the collection efficiency of the mirrors.

FY 2012 HIGHLIGHTS

We have demonstrated the m=2 neutron supermirror (graded-d-spacing NiC/Ti multilayer) deposition process on flat substrates made from nickel phosphorous alloy (the same material as the cylindrical mandrels used for the ENR process). The process has been verified to provide the neutron reflectivity expected for the NiC/Ti multilayer film. A TiN release layer has been successfully developed, and NiC/Ti multilayer replicas have been separated from flat masters coated with this release layer without multilayer structural degradation. The process has now been successfully transferred to the conical masters. We have also developed and successfully demonstrated a novel pulse plating technique, which provides improvements in spatial resolution for neutron mirrors fabricated from pure nickel.

Polarized ^{3}He in Neutron Scattering

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PROGRAM SCOPE

We are extending polarized neutron scattering into new domains by continued development and application of polarized ^{3}He spin-filters. These devices are particularly relevant to the Spallation Neutron Source, as the polarizing monochromators historically used at reactor sources will usually not be suitable polarizers, and wide-angle polarization analysis will be essential. We have developed neutron spin-filters based on the large spin dependence of the cross section for neutron capture by ^{3}He and applied these devices to small angle neutron scattering (SANS), reflectometry, and triple-axis spectrometry. Our developments have been adopted by the SNS and NIST Center for Neutron Research (NCNR) spin filter programs, with results merging. Implementation of wide-angle polarization analysis is the key thrust of our current activities.

FY 2012 HIGHLIGHTS

We have made progress towards wide-angle polarization analysis, in particular in the key area of analyzer cell fabrication. Our glass/optical shop has developed methods to fabricate wide-angle cells from GE180 glass. We have prepared six analyzer cells that can cover an angular range of 90 to 120 degrees. The relaxation times for these cells range from 100 to 400 hours. Based on neutron transmission measurements and electron paramagnetic resonance (EPR), we determined that the achievable ^{3}He polarizations are 65% to 80%. We have constructed an improved neutron-compatible solenoid that can operate at a higher field so that the relaxation times of our cells will not be compromised. For NMR-based inversion of the ^{3}He polarization in the polarizer cell, we have reduced the polarization losses in both the polarizer cell and the analyzer cell to $< 0.1\%$. A new, complete apparatus, consisting of the static field solenoid, polarizer and analyzer cells, a radio frequency solenoid, and NMR monitoring of the polarization in each cell, has been tested off-line and will be employed sometime during MACS commissioning in early 2013.

We continue to collaborate with the NCNR and SNS programs in neutron spin filters. A paper on the results from the first MACS experiment (November 2010) that used ^{3}He spin filters has been published [Phys. Rev. Lett. PRL 108, 107002 (2012)]. A paper on the improved wide-angle analysis apparatus has been submitted for the PNCMI 2012 conference. T.R. Gentile received the 2011 NIST Allen V. Astin Award for “excellence, innovation, and leadership in polarized ^{3}He research for applications in materials development and medical diagnostics.”

Magnetoelectric Hybrid Modes in Multiferroics: Neutron and Ellipsometry Studies

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Funding:	$220,000

PROGRAM SCOPE

Giant magnetoelectric effects in the recently discovered multiferroics open up an entirely new way of the phase control with potential for device applications in many areas, such as transducers, field sensors, data recording, etc. Magnetoelectric properties of multiferroics are closely associated with the collective nature of simultaneous magnetic and ferroelectric phase transitions. This project aims to reveal the features of the magnetic structure and the corresponding magnetic and lattice excitations underlying the giant effects associated with these transitions. A complementary combination of neutron scattering and far IR ellipsometry, together with closely coordinated crystal growth activity, has been used. Among the topics of this project are studies of the magnetoelectric properties of $BiFeO_3$, which is the only known room-temperature multiferroic with recognized potential for applications. Another direction of research is the far-infrared spectra of magnons and crystal field transitions in hexagonal $RE\text{MnO}_3$ (*RE*=Ho-Lu). Spectra of the hybrid modes that reveal both electric and magnetic-dipole activity are in the focus of our studies of *R*-iron garnets and orthorhombic $TbMnO_3$ crystals.

FY 2012 HIGHLIGHTS

Multiferroic $BiFeO_3$ attracts great interest because it works at room temperature. However, its magnetic structure, which is a key for its functional properties, remained uncharacterized. Using small-angle neutron scattering, we detected local ferromagnetism in $BiFeO_3$, confirming a long-standing prediction and demonstrating the potential of this material for applications (many of which require ferromagnetic order). We have also determined the strength of the magnetic interaction in $BiFeO_3$ using inelastic neutron scattering. Our data indicate that ferromagnetism can be also achieved in $BiFeO_3$ thin films, highlighting their potential for applications. Our experimental data also provide several key numerical parameters for theoretical analysis of this material. These results are expected to aid in design of future devices based on multiferroics.

Spontaneous magnetization of RE^{3+} ions at low temperatures changes the Mn^{3+} spin dynamics in hexagonal $RE\text{MnO}_3$ crystals (*RE* = Ho, Er, Tm, Yb, Lu). This phenomenon is related to a non-trivial interaction between two sub-systems of RE^{3+} and Mn^{3+} ions. Magnons in a frustrated 120° spin subsystem of Mn^{3+} have been studied using synchrotron radiation at the National Synchrotron Light Source. We discovered a systematic increase of the magnon frequencies with a decrease of the RE^{3+} ionic radius r_i and defined important parameters for spin exchange interaction and spin anisotropy that will be useful for a better understanding of the interplay between the antiferromagnetic and ferroelectric effects in these compounds.

Metastable Vortex Lattices - Properties and Applications

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Funding:	$174,000

PROGRAM SCOPE

When a superconductor is placed in a magnetic field, it is threaded by swirling whirlpools of electric current known as vortices. Understanding the vortex physics is important, as they are often the limiting factor for practical applications. At the same time, the vortices can serve as a probe into the nature of the superconducting state in the host material. In this project we study the vortex lattice (VL) using neutron scattering, focusing on two distinct goals: (1) the dynamics of metastable VL phases and (2) how the VL reflects an unconventional superconducting pairing symmetry.

The VL in MgB_2 displays an unusual degree of metatstability in connection with second-order transition, which cannot be understood in terms of the single domain free energy. Instead we proposed that this is due to jamming of counter-rotated VL domains, similar to the situation observed in granular systems.

We will investigate the dynamics of the transition to the VL ground state, which will provide information about the strength and distribution of VL domain boundaries and the activated behavior governing this transition.

The superconducting state emerges due to the formation and condensation of electron Cooper pairs. In materials such as UPt_3 and Sr_2RuO_4, the electrons in the pair are believed to form a triplet, and, in the former material, to give rise to three distinct superconducting phases. This adds significantly to the complexity of the problem; and, as a result, the exact nature of the order parameter in these compounds, which have become paradigms for unconventional superconductivity, is still largely unresolved. We will study the VL symmetry and form factor in both UPt_3 and Sr_2RuO_4 for different field orientations. We will investigate the effects of the magnetic field strength and temperature, and use creative field-temperature histories to prepare well-defined chiral states with different directions relative to the applied magnetic field. These studies will be complemented by neutron depolarization measurements of the bulk magnetization in UPt_3. Together our result will impose significant constraints on possible models of superconductivity in the two materials.

FY 2012 HIGHLIGHTS

The first paper reporting the metastable VL phases in MgB_2 was published. Extensive dynamical studies under the influence of AC excitations were carried out and are currently being analyzed. Studies of the bulk magnetization in UPt_3 were published, and VL studies for one field orientation are completed and are being compared to theoretical models for the superconducting penetration depth. For Sr_2RuO_4 VL, studies allowed the determination of the intrinsic superconducting anisotropy.

From Fundamental Understanding to Predicting New Nanomaterials for High-Capacity Hydrogen/Methane Storage and Carbon Capture

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Funding:	$0.00 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

On-board hydrogen/methane storage in fuel cell-powered vehicles is a major component of the national need to achieve energy independence and protect the environment. Fundamental breakthrough discoveries in materials science will be required to achieve light-weight, low-volume, safe, economical, and recyclable storage technology. The main obstacles in hydrogen storage are slow kinetics, poor reversibility, and high dehydrogenation temperatures for the chemical hydrides, and very low desorption temperatures/energies for the physisorption materials (MOF's, porous carbons). Carbon capture suffers from similar problems where the current technology is based on absorption in amine-based solvents which has limited reversibility and high regeneration cost. The solid-absorbers such as MOFs are not stable against real flue-gas conditions and/or do not have large enough CO_2 capture (i.e., working capacity) to be practical and cost effective.

The main scope of our research is to use neutron scattering methods along with first-principles computation to achieve fundamental understanding of the chemical and structural interactions governing the storage and release of hydrogen/methane and carbon capture in a wide spectrum of candidate materials. The main goals are to study the effect of scaffolding, nanosizing, doping of the candidate materials on their storage and dynamics properties, and to provide timely feedback and guidance from theory to de novo materials design and targeted syntheses throughout the DOE programs.

FY 2012 HIGHLIGHTS

Efficient Carbon Capture in Metal-Organics Frameworks (MOFs): Investigations of the application of MOFs to adsorptive carbon capture have focused on their appreciable storage capacities but fail to address the more pertinent issue of how MOFs perform under common industrial separation processes that are at the heart of carbon capture. Typical processes rely on swing adsorption and are limited to relatively low CO_2 partial pressures such that the total pore volume and the surface area are under-utilized. Here, we investigate the performance of a number of metal–organic frameworks with particular focus on their behavior at the low pressures commonly used in swing adsorption. This comparison clearly shows that it is the process that determines which MOF is optimal rather than there being one best MOF. In particular, using neutron scattering, we unrevealed the mechanism of carbon capture and found that MOFs that possess coordinatively unsaturated metal centers offer as much as 9 mmol/g swing capacity under certain conditions. This work will be an important guideline for deciding the best pair of carbon capture process and MOF material for optimum carbon capture.

Using Neutrons as a Probe to Study Magnetic Excitations in Strongly Correlated Electron Materials

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PROGRAM SCOPE

Understanding the interplay between magnetism and superconductivity continues to be a hot topic in modern condensed matter physics. The discovery of high-temperature superconductivity in iron-based materials in 2008 provided a unique opportunity to compare and contrast these materials with traditional high-T_c copper oxide superconductors. Neutron scattering plays an important role in determining the dynamical spin properties in these materials. This proposal is a continuation of a previous DOE-support proposal. This report summarizes the progress we have made over the past 12 months from Oct. 1, 2011, until Sept. 30, 2012. Overall, we continue to carry out extensive neutron scattering experiments on Fe-based materials, focusing on understanding how their magnetic properties interplay with superconductivity. In addition, we have established a materials laboratory at UT that has allowed us to grow these superconductors. Because neutron scattering typically demands a large amount of samples, by growing these materials in our own laboratory, we can now pursue neutron scattering experiments over the entire electronic phase diagram for both hole and electron-doped materials, focusing on regions of interests. The material synthesis laboratory at UT was established entirely with the support of DOE funding. We have made significant contributions in our understanding of the magnetic properties in Fe-based superconductors.

FY 2012 HIGHLIGHTS

We have carried out neutron scattering experiments to completely determine the spin wave excitations of the insulating iron-based material $Rb_{0.89}Fe_{1.58}Se_2$, which is published in *Nature Communications* [Nat. Comm. 2, 580 (2011)]. In addition, we have finished a long review article on magnetism in iron-based superconductors published in *Nature Physics* [Nat. Phys. 8, 709 (2012)]. We have started to work on Co-doped NaFeAs family of materials, which is made possible by BES support, and shall have many publications resulting from BES support in the coming years.

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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Funding:	$120,000

PROGRAM SCOPE

The fundamental process governing charging and discharging in energy storing battery electrodes is phase transition. For increased cyclic capacity, efficiency, and durability, electrodes for Li-cells must show fully reversible phase transformations upon Li extraction and insertion. Progress in this direction therefore depends on understanding the factors that enable or prevent such transformations under battery cycling conditions.

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 (1) can provide very high energy-storage capacity; (2) offer many phase transition paths (solid solution, intermetallic, displacement reactions, and ordering) representing most anode materials; and (3) present the greatest challenge in anode material science. In particular, the research will investigate (1) how the changes in particle size and composition of the electrodes affect/limit the phase transitions and cell degradation, (2) how the potential windows and charge/discharge rates affect the kinetics of phase transitions, and (3) the kinetics of formation of SEI layer in electrode-electrolyte interface. The research will be performed in collaboration with Dr. Xun-Li at Oak Ridge National Laboratory's SNS facility, 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. Nanoparticle electrodes have a high-density of nanoscale interfaces; and the research can lead to the discovery of optimum particle size, structure, and composition that yield highly reversible electrodes. The research will also enable the education and training of two graduate students in the new frontiers of battery material science.

Novel Collective States of Strongly Correlated Electron Systems

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Funding:	$206,000

PROGRAM SCOPE

Strongly correlated electron systems provide myriad opportunities to study novel electronic, magnetic, and structural phenomena that emerge out of strong interactions between electrons. Some of these phenomena are high T_c superconductivity, magnetic multiferroicity, and novel magnetic states such as quantum spin liquid. Our group has been studying several exemplary systems to identify the novel states and to understand the microscopic mechanism for those phenomena. Particular systems of our current interest are geometrically frustrated magnets such as two-dimensional kagome, three-dimensional pyrochlore (spinels), and quasi-two-dimensional kagome-triangular-kagome trilayer system SCGO; magnetic molecules such as Ni_4 and Mn_6; magnetic multiferroic $Sr_2FeSi_2O_7$; and unconventional superconductors such as the Fe- and Bi-based superconductors. For this research, our group utilizes elastic/inelastic neutron scattering techniques that directly probe static and dynamic properties of solid at the atomic length scale.

FY 2012 HIGHLIGHTS

Topological spin glass state of a quasi-two-dimensional frustrated magnet: We have presented a simple way of understanding the physics of the kagome-triangular-kagome trilayer antiferromagnet by mapping the complex magnetic interactions onto a problem of an ordered tricolor and a disordered binary sign degree of freedom. By doing so, we showed a systematic way of constructing different classical ground states and identified possible zero-energy excitations that involve ‘partial but extended’ number of spins in the system. We argued that due to the unique properties of the ground state, a topological spin glass is the ground state for the quasi-two-dimensional frustrated magnet.

Reference: K. Iida, S.-H. Lee, S-W. Cheong, “Coexisting order and disorder hidden in a quasi-two-dimensional frustrated magnet,” *Phys. Rev. Lett*. 108, 217207 (2012).

Emergent Phenomena in Novel Materials and Functionality Control: Characterization at Multiple Length and Time Scales

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PROGRAM SCOPE

The emergence of exotic states arising from the intricate coupling of the electronic and lattice degrees of freedom is a unique feature in strongly correlated electron systems. Such states 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; and unless new methodologies are implemented to describe such novel phenomena, the predictive capabilities of our theoretical tools will fail. A well-known example is that of a Mott insulator for which band theory predicts it to be a metal but is instead insulating. We now know that a combination of *d-d* correlations, charge transfer, and hybridization is what makes most transition metal oxides insulating. The goal of the proposed program is to explore such states of matter that appear to be endemic to oxide and intermetallic compounds.

In this program, we have focused on experimentally identifying the local microstructure, the distortions invoked by magnetic interactions, the effects of orbital hybridization and crystal phase transitions, local and global distortions, and their role in materials functionality and phase transitions in a wide class of materials. In this approach, we identify the nature of spin correlations and their role in spin-charge and -lattice interactions by varying temperature, magnetic field, pressure, and magnetic ion doping; and we characterize magnetic incommensurabilities by altering the chemistry of the material in question. Furthermore, we attempt to develop an understanding of how different electronic, magnetic, and structural order parameters compete and co-exist and how they can lead to phase separation. In doing so, we implement both neutron and x-ray scattering techniques at national and international facilities that allow us to probe structures and dynamics at different length and time scales.

FY 2012 HIGHLIGHTS

We have been continuing our work on the Fe-based superconductors and have recently identified a very important feature in the local structure of $K_xFe_{2-y}Se_2$ compounds that proves the structure, while in the superconducting state, is not phase-separated but is rather a hybrid phase where both magnetic and metallic Fe-Fe bonds are present. This is in fact consistent with recent findings reported in the cuprate superconductors. We find that the evolution of the Fe-Fe bonds across the phase boundary is continuous and there is clear absence of the structure presumed to be superconducting.

Self-Assembly of Conjugated Polymer Networks: A Neutron Scattering Study

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PROGRAM SCOPE

The principal objective of this program is to develop the fundamental understanding of self-assembly and network formation in systems of conjugated polymers dissolved in organic solvents through the use of advanced neutron and x-ray scattering techniques as non-invasive morphological probes. Small angle scattering experiments (SANS, USANS, SAXS, and WAXS) are performed to systematically evaluate self-assembly and network formation in systems of conjugated polymers over a broad range of length scales (0.1-10,000 nm). Through the use of these techniques, we systematically evaluate the structural effect of variations in important parameters such as the molecular structure of the polymer chains, the molecular weight, the solvent quality, and the temperature profiles that are used to drive self-assembly. These parameters are then correlated with changes to the fiber shape and to the large-scale network conformation (e.g., interconnectivity). Furthermore, we are also developing new in-situ SANS techniques that can directly correlate the evolution of the electronic properties with the changes to the structure of the gels. A novel emulsion processing method is also being developed to enable the coating of elastic conjugated polymer networks using traditional processing technologies (e.g., spray coating, doctor blading, and spin coating). Scattering experiments are also being conducted to evaluate the effect of spatial confinement of the self-assembling properties of the polymers inside the oil droplets at relevant length scales. Active layers generated from percolating conductive polymer networks are expected to generate a high density of nanometer sized p/n junctions that could efficiently transport charge and, in this way, improve the performance of polymer solar cells.

FY 2012 HIGHLIGHTS

We completed the development of the hardware necessary for dielectric-SANS measurements and subsequently performed the first experiments to correlate the evolution of poly-3-alkyl-thiophene (P3AT) organogels formed in different solvents. We have also systematically evaluated the effect of supersaturation on the structure and properties of the gels that are formed from different polymers. Working solar cell devices have also been fabricated from organogel dispersions that were also characterized with neutron scattering. In the next period, we plan to continue to increase our understanding of the physical parameters that control network formation and, for the first time, we aim to demonstrate the fabrication of working solar cells using purely electrostatic based assembly methods.

DOE National Laboratories

Correlations and Competition between the Lattice, Electrons, and Magnetism

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PROGRAM SCOPE

The properties of modern 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 different subsystems and the necessary conditions for enhancing or tailoring desirable physical properties has been identified as a Grand Challenge to the scientific community. Neutron and x-ray scattering are powerful probes that directly investigate the structural, electronic, and magnetic aspects of complex ground states, phase transitions, and corresponding excitations. Any one of the many different scattering techniques alone can reveal detailed information about the underlying physics. 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. The emphasis of close coupling between different scattering techniques and theory is the unique approach of this FWP.

FY 2012 HIGHLIGHTS

The FWP is currently investigating several important systems, such as the $A\mathrm{Fe}_2\mathrm{As}_2$ (A = Ca, Sr, Ba) and $R\mathrm{FeAsO}$ (R = rare-earth) families of high-temperature superconductors, $\mathrm{Li}M\mathrm{PO}_4$ (M = Fe,Co,Ni) magnetoelectric compounds, and $R\mathrm{FeO}_3$ and $R\mathrm{BaFe}_2\mathrm{O}_5$ (R = rare earth) based charge-ordered systems. Over the last year, our emphasis has turned to the study of different metal (M) substitutions in $\mathrm{Ba(Fe}_{1-x}M_x)_2\mathrm{As}_2$. We have examined the role that electron doping and impurity scattering play in both the suppression of AFM order and the appearance of incommensurate AFM order with M = Co, Ni, Cu. We find that Co and Ni follow the rigid band picture while Cu, with the strongest impurity scattering, does not. The strength of the Cu impurity scattering may also explain why SC is absent in this compound.

We have also investigated the nominally hole-doped series $\mathrm{Ba(Fe}_{1-x}\mathrm{Mn}_x)_2\mathrm{As}_2$. Mn doping induces a competing, possibly non-collinear, magnetic state for $x > 10\%$. Inelastic neutron scattering data for $x = 7\%$ show that Mn-doping gives rise to spin fluctuations from a competing checkerboard AFM state at wavevector $Q_{CB} = (1,0,1)$.

This fascinating behavior of the Mn-doped system has inspired investigations of the magnetic excitations in the parent $BaMn_2As_2$ compound, which is a local moment insulator with checkerboard AFM order. We have found that K substitutions induce metallic behavior in $BaMn_2As_{2;}$ however, strong AFM ordering (T_N > 500 K) remains, suggesting that charge conductivity and AFM order are independent of one another.

National School on Neutron and X-Ray Scattering

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Funding:	$232,000

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 2012 HIGHLIGHTS

The 14th National School on Neutron and X-ray Scattering was held from August 12th - 25th, 2012. Out of 222 applicants, 64 participants were selected to attend, of which 60 funded by this FWP. The participants spent the first week at Argonne National Laboratory and then transferred to Oak Ridge Laboratory on August 18th 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 (www.neutrons.ornl.gov/conf/nxs2012/ and www.dep.anl.gov/nx/).

Neutron and X-Ray Scattering

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Sr. Investigator(s):	Osborn, Ray, Argonne National Laboratory teVelthuis, Suzanne, Argonne National Laboratory Chmaissem, Omar, Northern Illinois University
Students:	2 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$2,028,000

PROGRAM SCOPE

The Neutron and X-ray Scattering Group investigates the structure and dynamics of bulk and interfacial materials with a particular focus on the role of phase competition in generating complex phenomena, such as superconductivity, magnetism, thermoelectricity, etc. The latest advances in neutron and x-ray instrumentation, 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 MSD.

FY 2012 HIGHLIGHTS

Our detailed investigations of the archetypal iron-based superconductors $BaFe_2As_2$ doped with potassium, sodium, or phosphor has provided the definitive phase diagram of $Ba_{1-x}K_xFe_2As_2$, evidence for a biquadratic coupling of the structural and magnetic order parameters, the first clear evidence that the energy of the spin “resonance” does not obey a postulated universal scaling form, the first observation of the incommensurability of the resonance due to the change in Fermi surface geometry, and strong evidence that nematic order results from Fermi surface nesting rather than orbital order.

We found direct evidence that the charge density wave transition in the canonical compound $NbSe_2$ is largely driven by the wavevector dependence of the electron-phonon coupling rather than a nesting-induced electronic instability as commonly assumed. We further observed unusual behavior of an acoustic phonon branch in a bilayer manganite at the onset of charge order, revealing a strong link between electron-phonon coupling and unusual physical properties, with possible implications to many other phenomena of interest.

Using polarized neutron diffraction, we determined the origin of the modulation of the resistance as the direction of a magnetic field applied to an interface between a cuprate superconductor and adjacent ferromagnet is changed. This detailed understanding is crucial towards utilizing such interface-induced ferromagnetism in oxide-based spintronic devices.

Gian Felcher, Argonne Emeritus Scientist and longtime member of the group, received the 2012 Sustained Research Prize of the Neutron Scattering Society of America for pioneering the development of neutron reflectometry.

Neutron Scattering

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Students:	0 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$2,150,000

PROGRAM SCOPE

This program is organized around the goal of decoding the mechanism(s) responsible for high-temperature superconductivity, with particular focus on the copper oxides, as well as newer systems, such as the iron-based superconductors. The main experimental tool is neutron scattering, 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, a new inelastic spectrometer with polarization analysis at the Spallation Neutron Source (SNS); it also participates in the U.S.-Japan Cooperative Program on Neutron Scattering, which largely utilizes spectrometers 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 2012 HIGHLIGHTS

The iron-based superconductor $Fe_{1+y}Se_xTe_{1-x}$ can be tuned between superconducting and magnetically-ordered ground states by varying the Se concentration. The parent material $Fe_{1.1}Te$ has magnetic moments on the Fe atoms that order antiferromagnetically at low temperature. Neutron spectroscopy performed at the SNS has revealed the surprising result that the Fe moments grow in magnitude when one heats the sample into the magnetically-disordered state, thus demonstrating a close coupling between local magnetic moments and the conduction electrons, one that may be important to the mechanism of superconductivity.

For copper oxide superconductors, there is a continuing debate on the relationship between magnetism and superconductivity, and the possible role of spatially modulated charge stripes. Scattering studies of the superconductor $La_{1.905}Ba_{0.095}CuO_4$ have now demonstrated that application of a magnetic field enhances charge stripe order as well as magnetic stripe order. Complementary measurements suggest a close connection between the stripe correlations and superconductivity.

Complex Electronic Materials

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Movshovich, Roman, Los Alamos National Laboratory
Ronning, Filip, Los Alamos National Laboratory
Sarrao, John L., Los Alamos National Laboratory
Yasouka, Hiroshi, Los Alamos National Laboratory
Students: 5 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding: $1,750,000

PROGRAM SCOPE

A delicate balance among competing interactions in strongly correlated electron materials leads to complex and collective quantum states with highly tunable functional responses on multiple length and time scales. This complex behavior is most pronounced near the magnetic/non-magnetic and metal/insulator boundaries in materials where electronic correlations are particularly strong. Especially interesting physics appears when these boundaries are tuned to absolute zero temperature, i.e., to a quantum-critical point. Research focuses on developing a fundamental understanding of complex electronic phenomena by discovering new examples of materials that reveal essential new physics. Developing this understanding requires a necessarily broad range of experimental techniques, often at extremes of low temperatures, high pressures, and high magnetic fields, that probe and tune static and dynamic spin-charge-lattice degrees-of-freedom and their interactions. Particular attention is given to highly correlated f-electron materials, where possible in single crystal form, as exemplary of the physics of complex electronic materials; but bridging lessons learned from their study to scientific problems posed by technologically relevant correlated d-electron materials is an important consideration. Collaboration with other DMSE projects and with external experimentalists and theorists benefits this research.

FY 2012 HIGHLIGHTS

We have discovered the nuclear magnetic resonance in ^{239}Pu, a signal that has resisted detection for over 50 years. This discovery opens a new era for understanding the most complex element in the periodic table as well as quantum states in materials based on Pu, e.g., the superconductivity that appears near a quantum-critical point in newly discovered $PuRhIn_5$. $PuRhIn_5$ is a member of the so-called 115 compounds that we have discovered and that exhibit a remarkable breadth of new physics. Unconventional superconductivity develops out of a quantum-critical state in one of those members, $CeCoIn_5$. We have shown that its superconductivity and other properties can be tuned reversibly by co-doping with electron and hole donors. One of those dopants, Cd, suppresses superconductivity and induces antiferromagnetic order. Pressure studies of Cd-doped $CeCoIn_5$ find that the global effect of Cd substitutions is reversible, but the formation of short-range magnetic droplets prevents the reappearance of the quantum-critical state in pristine $CeCoIn_5$. In collaboration with A. Yazdani, scanning tunneling spectroscopy has been used to visual for the first time the development of a heavy-fermion state in $CeCoIn_5$, a prototype of quantum entanglement. New techniques of time-resolved photoelectron spectroscopy, Larmor diffraction under pressure, and scanning magnetic-force microscopy also have been developed and applied to explore complex electronic materials.

LANSCE School on Neutron Scattering

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Students:	0 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$40,000

PROGRAM SCOPE

The Los Alamos Neutron Science Center (LANSCE) Neutron Scattering School was created in 2004. Since then, a LANSCE Neutron Scattering School has been held every year at Los Alamos National Laboratory. The school covers a variety of science topics where neutrons have made or can make a major impact. The main goal of the LANSCE Neutron Scattering School is to provide in-depth neutron-scattering training for each of the selected topics, predominantly to graduate students in their early stage of thesis research. A particular emphasis is put on selecting a diverse student body in order to foster a cross-institutional, cross-disciplinary, and multicultural learning environment. An implied goal is to grow a diverse user community in broad areas of neutron scattering.

FY 2012 HIGHLIGHTS

The 2012 LANSCE Neutron Scattering School was the 9th school in the series, and it was held September 12 - 21, 2012. The focus of the 2012 school was on the use of neutron scattering in soft matter, an area where neutrons have provided and continue to provide important insight into the structural properties and interactions of soft condensed matter with applications in energy, medical, and materials science. In addition, the 2012 school included a special track on crystallography for structural enzymology.

Center for Accelerating Materials Modeling

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

PROGRAM SCOPE

The Center for Accelerating Materials Modeling (CAMM) from Spallation Neutron Source (SNS) data aims to provide a software toolkit to integrate materials modeling and simulation with the analysis of experimental data taken at the SNS at Oak Ridge National Laboratory. Furthermore, it proposes to do so in a way that will allow a direct feedback loop (live or in near real time) between the modeling/ simulation and the experiment. A number of components are needed to achieve this aim; and in this seed project, we are constructing and demonstrating one of the core components of the software toolkit.

Specifically, this component is the software to refine potential (or force field) models in molecular dynamics simulations against data from inelastic/quasi-elastic neutron scattering experiments. We will demonstrate this software for two science projects from the “soft” and “hard” condensed matter domains, polyethylene oxide (PEO)–acrylic acid (AA) and $KTa_{1-x}Nb_xO_3$, respectively.

This toolkit will be extensible to a wide range of materials that can be studied by neutron scattering and will make a broad and significant contribution to materials modeling.

FY 2012 HIGHLIGHTS

CAMM is a new project with research efforts beginning in September 2012. The nature of the work in FY 2012 has therefore been that of a start-up phase. Initial workflows have been devised for the force field refinement against the neutron scattering data and are being evaluated using a small test case before scaling up to the two science projects.

Multiphasic Soft Colloids: Fundamentals to Application of Energy Sustainability

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Sr. Investigator(s):	
Students:	0 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$500,000

PROGRAM SCOPE

The central goal of this research program is to develop a fundamental understanding of the chemical and physical processes occurring on the microscopic length scale that are critical for the molecular-level design of multiphasic soft colloidal systems with desirable macroscopic functionality. This class of structurally heterogeneous materials has great promise as a platform for energy-related applications, including light harvesting, organic light emitting diodes, photonic bandgap devices, and supercapacitors. To address the overarching goals, 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 on elucidating the relationship between dynamics and structure on both local and collective length scales that give rise to rich equilibrium and non-equilibrium phase behavior. These two specific aims, providing critical links between the bulk material properties in their functional form and the microscopic features of their precursor liquid state, are all underpinned by specific tailored synthesis of targeted systems designed to optimize the experimental methodology. These goals will be achieved by a synergistic approach integrating three unique research strengths of ORNL: the neutron scattering tools at the SNS, computational resources at the NCCS, and material synthesis at the CNMS. The knowledge gained from this program will provide scientific insight into fundamental guidelines for sustainable energy-related applications of multiphasic soft colloids that will impact a broad range of DOE's needs in its energy mission.

FY 2012 HIGHLIGHTS

This project was funded beginning July 2012. We initiated the construction of a computational algorithm to describe biphasic colloids and began the preliminary atomistic simulation testing using the Oak Ridge Institutional Cluster at SNS to provide the microscopic intra-colloidal structural information and its dependence on structural asymmetry. A parallel theoretical calculation based on a coarse-grained mean field model and complemented by Monte Carlo simulation is also being conducted to provide the inter-colloidal spatial arrangement at mesoscopic length scales. A visiting scientist has also been appointed to synthesize the targeted biphasic colloidal system at ORNL's CNMS beginning September 2012. Substantial research progress of this project in terms of theory, simulation, and material synthesis and publications are expected in the next few months. We have also submitted several neutron and x-ray beam time proposals to different user facilities, such as SNS, NCNR, APS, NSLS, ILL, Spring8, and ESRF, to conduct the comparative experiments.

Physical Behavior of Materials

Institutions Receiving Grants

High Performance Bulk Thermoelectric Materials	
Institution:	Boston College, Trustees of
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Principal Investigator:	Ren, Zhifeng
Sr. Investigator(s):	
Students:	1 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$150,000

PROGRAM SCOPE

High performance bulk thermoelectric materials that can work at temperatures between 300°C and 800°C are the focus of this project. We focus on both thermal conductivity reduction and power factor enhancement. We propose to focus on p-type half-Heuslers that have high thermoelectric power factors. Such high power factors give us a better chance to make the ZT higher by reducing the thermal conductivity via composition tuning and nanostructures creation. In addition to thermal conductivity reduction, we will also explore the possibilities for further power factor enhancement by using resonant doping and energy filtering. We also propose to study solar radiation absorbing materials to be used together with the thermoelectric materials for efficient solar energy conversion into heat and electricity.

FY 2012 HIGHLIGHTS

We first improved the ZT from 0.8 in $Hf_{0.5}Zr_{0.5}CoSb_{0.8}Sn_{0.2}$ to 1.0 in $Hf_{0.8}Ti_{0.2}CoSb_{0.8}Sn_{0.2}$ by replacing Zr with Ti due to lower thermal conductivity because of the larger atomic mass and size difference of Hf and Ti than Hf and Zr. However, the Hf concentration increased from 0.5 to 0.8, which increases the cost since Hf is more than 10 times expensive than any of the other elements. The challenge was to decrease the concentration of Hf. What we found is that we could replace a little bit of Hf and Zr with Ti. The best composition we found is $Hf_{0.44}Zr_{0.44}Ti_{0.12}CoSb_{0.8}Sn_{0.2}$ with a ZT of 1.0 but less Hf concentration.

Metamaterials as a Platform for the Novel Materials for Energy Applications

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Principal Investigator: Padilla, Willie
Sr. Investigator(s): Bingham, Chris, Boston College, Trustees of
Students: 0 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding: $100,000

PROGRAM SCOPE

The recent advent of metamaterials (MMs) has given rise to dramatic new electromagnetic responses and 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, and materials science to nanoscience. The Metamaterial perfect absorber has the potential to provide realizable benefits to a wide range of devices. Key among them is their use in energy harvesting applications when used in conjunction with thermal photovoltaics (TPV). Kirchhoff's law of thermal radiation states that the emissivity of a body is equal to its absorptivity. Thus the metamaterial perfect absorber will then also have a corresponding well defined emissivity. By tailoring the emissivity to match the band gap of a TPV material, the overall efficiency of the system can be improved. The proposed research activities emphasize the computational design and fabrication of the materials, and the characterization of their electromagnetic properties.

FY 2012 HIGHLIGHTS

We have studied the history of absorbing materials and their evolution into present day designs and possibilities for future applications. A key area of focus was in furthering the development of the MMPA design methodology, including how constituent materials and overall dimensions affect the overall absorptivity. Through this understanding, the metamaterial perfect absorber can be effectively transitioned into real devices. The models and tools developed provide the foundation for the development of a new class of materials for energy harvesting applications and beyond.

Hybrid Inorganic Nitride Organic Semiconductor Heterostructures

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Students: 0 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding: $210,000

PROGRAM SCOPE

We seek to explore a new class of hybrid inorganic-organic semiconductor media with an internal organization on the nanometer scale, as composite material structures which physically integrate crystalline III-nitrides and selected organic semiconductors. The key approach in this program is the conformal deposition of conjugated organic semiconductors unto the nitride nanostructures, for enabling electrical interconnects as well as modifying the coupling between electronic and electromagnetic states. The research includes novel methods of nanostructured material synthesis, fundamental studies of electron and hole transport across InGaN and selected organic systems, with the application goal of enabling the mesoscopic configurations of functional GaInN nanostructures toward their embodiment in visible optoelectronic devices. Scientific interest and promise arises from the fact that some of the basic physical attributes of III-nitride and (opto)electronically important organic materials are qualitatively as well as quantitatively quite different, such as carrier mobility, which may differ by several orders of magnitude. Yet, both III-nitrides and selected organic semiconductors have large optical oscillator strengths, though a fundamental difference exists between the physical nature of the corresponding electronic excitations (extended Wannier and molecular Frenkel excitons, respectively). The contrasts, attributes, as well as limitations of each material system drive our intention to explore the basic science and physical properties of III-nitride/organic semiconductor heterostructures. The key question we wish to answer in the affirmative is *Does material integration of III-nitrides and organic semiconductors, on the nanoscale, yield material synergy which leads into higher (opto)electronic performance of the joint "intercalated" material than the simple sum of its parts?* Our longer term aspirations include exploiting the hybrid properties for established applications (such as solid state lighting) and for entirely new innovative device concepts that might arise from the combination of joint electronic and optoelectronic properties from such material synergy.

Plasmonic Photovoltaics

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Sr. Investigator(s):	
Students:	0 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding:	$150,000

PROGRAM SCOPE

The objective of this program is to understand the role of plasmonic and metallodielectric nanoscale structures in solar and optical energy conversion. A major focus of the current effort is on description of light trapping in nanostructured thin film absorbers. Thin film photovoltaic structures with nanophotonic light trapping elements can exhibit a significantly enhanced local density of optical states relative to homogeneous bulk absorber materials. This leads to a local enhancement of optical intensity, absorption and spontaneous emission in the absorber layer. Nanophotonic structures can also modify the incoupling of sunlight into solar absorber layers. Plasmonic structures enable a very high degree of light confinement relative to purely dielectric materials; but light confinement is also accompanied by optical losses in the metallic layers, which is parasitic with respect to light absorption in semiconductor absorber layers. Theoretical work is concentrated on determining the limits to light absorption in nanostructure materials using the local density of states framework. We find that nanoscale structures exhibit both localized Mie resonances and propagating Bloch modes and that both the size and shape of individual nanostructures, as well as their short-range and long-range order, affect light coupling into Mie resonance modes and Bloch modes. More broadly, we seek to connect a wave-optical description of light-matter interaction in nanoscale structures to well-known ray-optical limits to light absorption in bulk materials. Experimental work is focused on design and fabrication of well defined plasmonic and metallodielectric nanoscale absorber structures using soft imprint lithography methods, as well as characterization using quantitative structural and optical measurements. The power spectral density of surface roughness is derived from atomic force microscopy, and its role on light absorption is determined using angle-resolved internal photocarrier collection efficiency measurements. The long-term impact of this work is in enhancement of the operating voltage, solar photocurrent, and conversion efficiency in thin film solar cells.

FY 2012 HIGHLIGHTS

We have used the localize density of state description to predict the limits to light trapping and optical intensity enhancement in a wide variety of nanoscale photonic structures (dielectric thin films, surface plasmon polariton waveguides, plasmon slot waveguides, photonic crystals, and plasmonic antenna arrays); and we demonstrated specific absorber designs that exhibit light trapping beyond ray optical limits. We demonstrated experimentally the role of scatterer shape, long range order, and short range order on light trapping and photocurrent enhancement for plasmonic scatterers in thin film amorphous silicon photovoltaic structures.

Functional Domain Walls as Active Elements for Energy Technology

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Sr. Investigator(s):	
Students:	1 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$150,000

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 2012 HIGHLIGHTS

We have synthesized free-standing, ultra-long, single-crystal VO_2 and doped VO_2 nanowires at ultra-high densities [APL, 100, 103111 (2012)], and high-quality, textured VO_2 thin films using pulsed laser deposition on nearly arbitrary substrates (submitted 2012). These would enable fabrication of a wide range of VO_2 devices at large areas, as well as free-standing VO_2 membrane if the substrate is selectively etched away.

Using these materials, we have also developed nanoscale, solid-state thermometers and powermeters by exploiting the thermally-driven phase transition in VO_2 nanowires near room temperature [ACS Nano, 5, 10102 (2011)] and giant-amplitude, high-work density microactuators with phase transition activated nanolayer bimorphs [Nano Lett. in press (2012)].

RECOVERY ACT - Evaluating the Oxidative, Photothermal and Electrical Stability of Colloidal Nanocrystal Solids

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Sr. Investigator(s):	
Students:	0 Postdoctoral Fellow(s), 2 Graduate(s), 1 Undergraduate(s)
Funding:	$0.00 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

IV-VI nanocrystal solids are a novel class of granular electronic materials with great technological potential (e.g., photodetectors, FETs, 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: (1) the use of robust molecular surface ligands, (2) the conformal coating of NC films with thin inorganic shells grown by room-temperature atomic layer deposition, and (3) in situ creation of core-shell NC solids by low-temperature solution-based ion exchange.

FY 2012 HIGHLIGHTS

We have expanded our successful atomic layer deposition (ALD) infilling strategy to develop a new, all-inorganic matrix engineering approach to achieve record electron mobility and environmental stability of lead selenide (PbSe) quantum dot (QD) films for use in next-generation solar cells. We published a paper describing the use of low-temperature atomic layer deposition (ALD) infilling as an effective method to improve the performance and stability of nanocrystal-based electronic devices, including field-effect transistors and solar cells. We are continuing to carry out the project plan as outlined in our original proposal by using Scanning Kelvin Probe Microscopy (SKPM) and Electrostatic Force Microscopy (EFM) to characterize the electric field distribution of QD solar cells operating under bias as a function of oxidation, temperature and illumination. The goal is to develop the ability to map the band diagrams of operating QD solar cells using and study the electronic impact of oxidation and other stressors as they occur in real time.

Study of p-Type ZnO and MgZnO Thin Films for Solid State Lighting

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Funding:	$120,000

PROGRAM SCOPE

The goal of this project is to gain complete knowledge on p-type Sb-, Ag-, and N-doped zinc oxide (ZnO) and magnesium zinc oxide (MgZnO) thin films by plasma-assisted molecular beam epitaxy. Semiconductor light emitting diodes (LEDs) are an energy-saving alternative to incandescent and fluorescent light. Besides the traditional gallium nitride for solid state lighting, ZnO materials are receiving significant attention due to their unique properties such as wide band gap and large exciton binding energy. Although p-type has been observed from ZnO-based materials doped with many dopants, the choice of dopant remains controversial and the reliability of reported p-type ZnO is still poor. In this project, we will carry out the following tasks: (1) developing low background electron-carrier-density, single-crystalline thin films using suitable buffer layers; (2) achieving reliable p-type ZnO and MgZnO on sapphire by tuning growth conditions and studying p-type thin films through various experimental methods; and (3) understanding the mechanism of Sb-, N-, and Ag-doping in p-type ZnO and MgZnO. The successful demonstration of the research will mark a step closer toward the development of commercially viable LEDs based on ZnO and MgZnO materials for solid state lighting.

FY 2012 HIGHLIGHTS

Thus far, we have achieved low background electron carrier concentration of ZnO thin films below ten to the seventeenth using suitable buffer layers; we have achieved high-quality MgZnO thin film samples with magnesium content between 0 and 0.2 and have started to study the p-type doping of MgZnO films; we have also grown many Ag-doped ZnO thin films and found that p-type films are very difficult to obtain although weak p-type behavior out of some of these films was demonstrated. Furthermore, we have successfully demonstrated p-type characteristics of Sb-doped ZnO thin films by characterizing p-n-p ZnO device structures. In the next period, we continue to find controllable growth process to obtain p-type ZnO and MgZnO thin films.

Using Neutron as a Probe to Study Magnetic Excitations in Strongly Correlated Electron Materials

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Sr. Investigator(s):	
Students:	0 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding:	$130,000

PROGRAM SCOPE

Understanding the interplay between magnetism and superconductivity continues to be a hot topic in modern condensed matter physics. The discovery of high-temperature superconductivity in iron-based materials in 2008 provided a unique opportunity to compare and contrast these materials with traditional high-T_c copper oxide superconductors. Neutron scattering plays an important role in determining the dynamical spin properties in these materials. This proposal is a continuation of a previous DOE-support proposal. This report summarizes the progress we have made over the past 12 months from Oct. 1, 2011, until Sept. 30, 2012. Overall, we continue to carry out extensive neutron scattering experiments on Fe-based materials, focusing on understanding how their magnetic properties interplay with superconductivity. In addition, we have established a materials laboratory at UT that has allowed us to grow these superconductors. Because neutron scattering typically demands a large amount of samples, by growing these materials in our own laboratory, we can now pursue neutron scattering experiments over the entire electronic phase diagram for both hole and electron-doped materials, focusing on regions of interests. The material synthesis laboratory at UT was established entirely with the support of DOE funding. We have made significant contributions in our understanding of the magnetic properties in Fe-based superconductors.

FY 2012 HIGHLIGHTS

We have carried out neutron scattering experiments to completely determine the spin wave excitations of the insulating iron-based material $Rb_{0.89}Fe_{1.58}Se_2$, which is published in *Nature Communications* [Nat. Comm. 2, 580 (2011)]. In addition, we have finished a long review article on magnetism in iron-based superconductors published in *Nature Physics* [Nat. Phys. 8, 709 (2012)]. We have started to work on Co-doped NaFeAs family of materials, which is made possible by BES support, and shall have many publications resulting from BES support in the coming years.

Frequency Dependent Properties of Magnetic Nanoparticle Crystals

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Funding:	$155,000

PROGRAM SCOPE

The goal of this project is to measure the magnetic permeability and electric permittivity of ordered nanoparticle assemblies over frequencies ranging from Hz to GHz. The main hypothesis is that the high frequency performance of composite materials has been limited because of the range of relaxation times; if a composite is a dipolar ferromagnet, the magnetic moments will respond collectively like a single-phase material. If the composite has high magnetization nanoparticles embedded in an insulating matrix, it can ideally have higher permeability than ferrites and avoid the significant eddy current power losses of magnetic metals and alloys. We have shown that porosity, variations in particle size, and variations in interparticle separation all lead to a range of local effective magnetic fields that in turn lead to a broad range in relaxation times, but that porosity is the most critical factor to control. This will be done by using self-assembled nanoparticle crystals, where particles of uniform size form dense, ordered compacts with controlled solvent evaporation. The low frequency behavior will be measured with SQUID magnetometry and AC susceptibility. The results will screen samples for undesirable spin glass-like behavior, where the coupling among particles is not homogeneous and there is a broad range of relaxation times. To measure the response at moderate (MHz) and high (GHz) frequencies, we have acquired an Agilent Technologies E5071C vector network analyzer. From the reflected and transmitted waves as a function of frequency, the impedances and the complex permeability and permittivity are determined. The permeability will show whether the composites act as dipolar ferromagnets and have a characteristic blocking frequency. The permittivity will indicate the frequency range where the capacitive reactance between conducting particle cores becomes significant, and where more strongly insulating barriers are necessary. In the highest frequency range, we will examine the effect of dipolar ferromagnetism on the width of the ferromagnetic resonance peak and look for evidence of spin wave confinement and magnonic crystal effects.

FY 2012 HIGHLIGHTS

The work thus far has focused on the design and testing of the apparatus for high frequency measurements. In order to minimize losses and reduce artifacts, it is critical that the transmission line from the network analyzer to the sample maintains a 50 ohm impedance. The sample is loaded into a toroidal cell that is inserted into a coaxial transmission line; but since the sample diameter is larger than the cable, the expansion stages must be carefully designed and symmetrically balanced between the network analyzer ports measuring the reflected S_{11} and transmitted S_{21} signals. We have done preliminary tests on bulk powders and disordered assemblies of carbon-coated cobalt nanoparticles.

Crystallization and Thermoelectric Transport in Silicon Microstructures and Nanostructures under Extreme Electrical Stress

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Funding:	$128,000

PROGRAM SCOPE

(1) Study crystallization of silicon structures at small scales and evaluate the possibility of using pulsed electrical stress to achieve single crystal domains with preferred crystal orientation from lithographically defined Si thin films deposited on arbitrary substrates.

(2) Conduct basic research on thermoelectric phenomena in silicon microstructures and nano-structures under extreme electrical stress (which play an important role in the crystallization process).

Our experimental studies (a) show that silicon wires melt and re-solidify with significant changes in physical properties when sufficient power is applied; (b) suggest formation of two single-crystal silicon domains along each wire and that preferred crystal orientation may be achieved in suspended structures; and (c) indicate that strong thermoelectric transport is involved in the self-heating process under extreme electrical stress (observed as highly asymmetric heating and melting of the structures, depending on the current direction). Single-crystal may be formed because the wires cross-section is smaller than the thermodynamically favored grain size. Extreme electrical stress in these small-scale structures results in current densities on the order of 10^7-10^8 A/cm^2 and temperature gradients on the order of 1 K/nm. Detailed electrical, physical (SEM, TEM, and high spatial and temporal resolution optical observations of light emission), and thermoelectric analysis of films and structures before, during, and after electrical stress will be performed. Experimental results will be compared to physical models through numerical simulations to gain understanding of the processes involved and to predict electrical stress conditions for desired crystallization results.

FY 2012 HIGHLIGHTS

(1) A more complete analysis is performed on the high temperature electronic and thermoelectric phenomena. The contribution of generation, transport, and recombination of minority carriers to thermoelectric heat is found to be the dominant mechanism leading to the observed self-heating asymmetries. (2) A procedure is developed to extract high-temperature electrical resistivity, ρ(T) and thermal conductivity, k(T) of nano-crystalline (nc) Si using iterative simulations varying ρ(T) and k(T) to match experimental I-V characteristics of nc-Si microwires as they are self-heated to melting. (3) Computational models are being improved for more efficient and accurate models that account for the granularity that leads to percolation and nano-scale filament formation during self-heating. (4) Improvements are made on the high-temperature thin film Seebeck measurement setup to allow more reliable simultaneous S-T and R-T measurements in the 30 C - 600 C range, and a new high-temperature Hall mobility setup is being developed.

Charge Transfer Across the Boundary of Photon-Harvesting Nanocrystals

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Funding:	$157,000

PROGRAM SCOPE

The goal of this project is to understand the fundamental processes that govern interfacial charge transfer across nanocrystal (NC) boundaries. We will carry out use-inspired fundamental studies of charge transport from NCs into other semiconductor materials with two principal goals: (1) to understand and control electronic structure and transport properties across NC interfaces and (2) to create confined-but-connected nanostructures that balance quantum-confinement and –coupling for optimized light capture and charge transport. Major themes will include the role of dimensionality in charge and energy transport and the physical and chemical properties of nanocrystal surfaces. The work will be 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 will combine silicon and solution-synthesized NCs in inexpensive, efficient solid-state solar cells.

FY 2012 HIGHLIGHTS

We have measured charge transport in films of ligand-free nanocrystals designed to have strong electronic coupling, and analyzed the results with a model based on grain-boundary scattering. In addition, we have demonstrated that room-temperature sputtering can produce inorganic electron- and hole-transport layers for prototype photovoltaic devices. Thus far, we have made devices with approximately spherical NCs; but we have also begun to make thin films with semiconductor nanorods, which offer some potential advantages over NCs. Finally, we have completed the initial design of a high-pressure probe/reaction cell that can produce realistic reaction conditions and fast cycle times for atomic layer deposition, which will be used to infiltrate thin films of semiconducting NCs with inorganic materials.

Complex Amorphous Transition-Metal Dielectrics

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Funding:	$190,000

PROGRAM SCOPE

We are studying structure/property relationships in electronic insulators using high-throughput experimental methods. In this approach, we synthesize composition-spread thin films using spatially-separated sources to create a lateral gradient in the average composition of atomically-mixed elements. Interrogating these composition spreads allows rapid determination of composition-dependent properties. At present, we are directing our efforts in two main threads:

(1) Identifying and understanding amorphous oxides with a high dielectric constant. These materials could play a role in advanced electronics technology. Previous studies have focused on a few chemical systems; the advantage of our approach is that we can efficiently explore the properties of a very wide range of compositions, including ternary oxides (three cations and oxygen). In order to discern trends, we can readily measure and compare the density, dielectric constant, optical refractive index, vibrational modes, and other properties with a composition resolution of about one percent in each cation. We are presently extending our studies to low-temperature measurements in order to more completely understand the nature of the materials.

(2) Developing the techniques needed to characterize ionic conductivity in oxides in a high-throughput manner. Oxides with a high O-ion conductivity could be useful in large scale high-temperature fuel cells or small-scale intermediate-temperature fuel cells for portable applications. We use impedance spectroscopy to infer the oxygen-ion conductivity within the grains of a polycrystalline thin film. We have developed and now validated an approach that is compatible with high-throughput requirements. We expect this approach to be useful for characterizing Li-ion and Na-ion conductivity as well, enabling discovery of new electrolyte materials that could dramatically increase the safety and reliability of batteries.

FY 2012 HIGHLIGHTS

We have identified a new material—amorphous tantalum oxide with a small amount of germanium oxide added—that has a 35% higher dielectric constant than pure tantalum oxide. The behavior apparently reflects a unique change in bonding of the atoms. We have now confirmed that analogous behavior does not occur, for example, in the case of silicon substituted in tantalum oxide nor for germanium substituted in hafnium oxide. Amorphous tantalum germanium oxide could lead to improvements in electronics, such as higher performance transistors or higher density memory technology.

Using Interfaces to Create Strongly-Coupled Magnetic Ferroelectrics via Atomic-Scale Heteroepitaxy

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Funding: $350,000

PROGRAM SCOPE

In this program, we are developing the scientific ideas necessary to apply a materials design paradigm to the creation of multiferroics with unprecedented coupling between ferroelectric and magnetic order parameters, i.e., strongly-coupled magnetic-ferroelectrics. This project has two research objectives. The first 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, but we recently predicted a class of materials that we call hybrid improper ferroelectrics where octahedral rotations are exploited to enable such switching. 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. Our second objective is to create magnetic ferroelectrics where the magnetism can be turned on by applying an electric field. Such an effect has also never been demonstrated, but we predicted it to occur in appropriately strained $EuTiO_3$. Our subsequent observation of a strain-induced ferromagnetic ferroelectric state in strained $EuTiO_3$ confirms the microscopic coupling model and calculations underlying this prediction. The simultaneously ferromagnetic and ferroelectric state that we induced in $EuTiO_3$ with strain created the world's strongest ferromagnetic ferroelectric, in agreement with our first-principles prediction. This verification strongly motivates our desire to turn on the strong ferromagnetism in appropriately strained $EuTiO_3$ by the application of a modest electric field. By creating new interface phases and atomically thin layers, we are achieving, through rational design, materials systems that provide the structural and magnetic properties—which are often mutually incompatible in bulk systems—needed to realize such a strongly coupled magnetic-ferroelectric.

FY 2012 HIGHLIGHTS

Using first principles calculations, we showed that the strong coupling between the rotations of oxygen coordination octahedra in complex oxides (a type of lattice distortion that is ubiquitous in complex electronic materials) and magnetic properties represents an opportunity to understand and create new multiferroics. We established general design rules and identified new classes of materials (i.e., known Ruddlesden-Popper phases as well as artificial superlattices) that should exhibit such behavior. Our work showed, for the first time, how octahedral rotations simultaneously induce and thereby naturally couple ferroelectricity, magnetoelectricity, and ferromagnetism—a breakthrough in the field of multiferroics. The new octahedral-rotation-based mechanism enables an applied electric field to globally and deterministically switch the magnetization by 180° in a single-phase multiferroic material.

Following our materials-by-design approach, we have grown epitaxial thin films of the materials identified by reactive molecular-beam epitaxy and are characterizing their structure and properties. One of the experimental issues that we have run up against is the difficulty in switching the materials we have made to date through the application of an electric field. This difficulty has motivated our theory effort to identify materials within this new class of multiferroics having lower activation barriers to switching.

Prediction of Thermal Transport Properties of Multiscale-Structured Crystalline Materials

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Funding:	$150,000

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 mutliscale 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 will 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 2012 HIGHLIGHTS

Thus far, we have derived the balance equation of linear momentum with the atomistic information, i.e., the arrangements and interactions of atoms in a crystal, being built in the formulation. Our preliminary code has demonstrated that, with 99.4% reduced degrees of freedom compared with MD, the concurrent atomistic-continuum (CAC) method allows dislocation loops to grow up to ~75 nm in radius, comparable with that observed in experiments and significantly larger than that have been modeled in existing MD simulations. We have also investigated the formation and propagation of defects in SrTiO3 crystal, a potential thermoelectric material. Our CAC simulation results have demonstrated a smooth passage of cracks and dislocations through the atomistic-continuum interface without need of additional constitutive rules or special numerical treatment. The stacking fault width and nanoindentation hardness measured in the CAC simulations agrees well with existing experimental data.

Interfaces in Electronic and Structural Materials

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Funding:	$129,000

PROGRAM SCOPE

The objective of this project is to advance fundamental understanding of materials interfaces, especially under extreme conditions of large deformations and high temperatures, and to develop new methods for computational prediction of interface properties. Some of the specific topics of the proposed research include (1) investigation of the effect of crystallographic characteristics, applied stresses and high temperatures on thermodynamic characteristics, and mechanical strength of internal interfaces; (2) dynamics and mechanisms of grain rotation at the nanoscale; (3) interaction of moving grain boundaries with dislocations; and (4) nucleation and growth of new grains in nano-twinned materials. These topics are centered around the general problem of thermodynamic stability of interfaces as part of materials microstructure.

The proposed approach to achieving the stated goals is a combination of theory and atomistic computer simulations, primarily molecular dynamics and a variety of Monte Carlo techniques. The atomistic approach will be combined, in a synergistic manner, with the phase-field crystal method allowing to extend the simulations to greater length and time scales. Al, Au, Cu, Co, and Fe will be studied as model metallic materials.

FY 2012 HIGHLIGHTS

(1) We have studied the phenomenon of GB premelting observed at high temperatures approaching the melting point of the material. The proposed a thermodynamic model of this process is based on the sharp-interface approximation with a disjoining potential. Contrary to the classical nucleation theory, the model predicts the existence of a critical temperature of superheating and offers a simple formula for its calculation. The model has been successfully tested against molecular dynamic simulations in which liquid nuclei at a superheated boundary were obtained by an adiabatic trapping procedure.

(2) We have developed a rigorous thermodynamic theory of plane coherent solid-solid interfaces in multicomponent systems subject to non-hydrostatic mechanical stresses. The theory includes rigorous and accurate expressions for the interface free energy as an excess quantity and a generalized adsorption equation. The interface stress tensor and the interface excess shear emerge naturally from this equation as an appropriate excesses over bulk properties. The theory has been applied to atomistic simulations of a symmetrical tilt GB in Cu and Cu-Ag alloys using a combination of molecular dynamics and Monte Carlo methods.

(3) We proposed general analytical expressions relating equilibrium fluctuations of the GB shape and position to key parameters governing its motion coupled to a shear deformation. We have validated these expressions by molecular dynamics simulations for tilt boundaries and demonstrate how they can be used to extract the misorientation-angle dependence of the GB mobility. This work advances the

current understanding of GBs and their role in materials behavior in extreme thermo-mechanical environments relevant to energy applications.

Quantum Nanoplasmonics Theory

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Funding:	$143,000

PROGRAM SCOPE

The program is aimed at fundamental theoretical investigations of a wide range of phenomena where quantum properties of matter and surface plasmon excitations are of primary importance. Among phenomena where quantum behavior of surface plasmons defines their fundamental physics is spaser (quantum generation and amplification of nanoscopic optical fields). An example of such a phenomenon is the recently predicted effect of metallization of dielectrics [Phys. Rev. Lett. 107, 0866021-5 (2011)] or spaser [Phil. Trans. R. Soc. A 369, 3510-3524 (2011)]. Matter in ultrastrong and ultrafast optical fields is another research field of this program where quantum phenomena play dominating roles [Nat. Phot. 5, 677-681 (2011); Appl. Phys. Lett. 100, 051904-4 (2012)].

FY 2012 HIGHLIGHTS

We have investigated, both theoretically and experimentally, the attosecond electronic process in a dielectric solid induced by ultrastrong and ultrafast laser pulses [Nature, (In Print) (2012)]. Subfemtosecond solid-state spectroscopy of the underlying electron processes reveals the feasibility of manipulating the electronic structure and electric polarizability of a dielectric with the electric field of few-cycle near-infrared (NIR) light. We irradiate a dielectric (fused silica) with a waveform-controlled NIR several-V/Å few-cycle light pulse and probe changes in extreme ultraviolet (XUV) absorptivity and NIR reflectivity on a sub-femtosecond to few-femtosecond time scale. The field-induced changes follow, in a highly nonlinear fashion, the turn-on and turn-off behavior of the driving field, in agreement with the predictions of a quantum mechanical theory. The ultrafast reversibility of the effects implies that physical properties of a dielectric can be controlled with the electric field of light, offering the potential for petahertz-bandwidth signal manipulation.

Fundamental Piezotronic and Piezo-Phototronic Effects in Nanowires

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Funding:	$137,000

PROGRAM SCOPE

The goal of this project will be to investigate and utilize fundamental piezotronic and piezo-phototronic effects in nanowires for developing novel electromechanical devices and interfaces between machine and human/environment. For Wurtzite-structured materials lacking central symmetry, such as ZnO, GaN, and InN, piezopotential is created in the crystal upon straining. Owing to the semiconducting and piezoelectric properties of these materials, the strain-created inner-crystal piezopotential can serve as "gate voltage" to effectively modulate charge transport across interface/junction in as-fabricated devices. This is the piezotronic effect, and electronic devices fabricated based on this general mechanism are piezotronics [Adv. Mater. 24, 4632-4646, (2012)]. Additionally, piezo-phototronic effect is the tuning and controlling of charge carrier generation, separation, or recombination at a *p-n* junction by piezopotential, which can be used to effectively improve the performance of LEDs, solar cells, and photodetectors [Adv. Mater. 24, 4632-4646, (2012)]. Much of the preliminary theoretical investigation for distribution of piezopotential and its modulation effect in electronic and optoelectronic processes have been developed by our group [Adv. Mater. 23, 3004-3013, (2011); Adv. Mater. 24, 4712-4718, (2012)]. It is our goal to develop and modify more sophisticated theoretical framework along with experimental work. Central to our design are 1D Wurtzite-structured nanomaterials, with enhanced piezoelectric and mechanical properties compared to their bulk counterparts, which are crucial for investigating piezotronic/piezo-phototronic effect and developing devices with characteristics such as superior sensitivity and responsivity. We have demonstrated the reproducible synthesis of 1D Wurtzite-structured ZnO nanowires with controlled morphology/properties, either in free-standing or ordered array form [Science 291, 1947-1949, (2001); Nano Lett. 10, 3414-3419, (2010)].

In these proposed experiments, we will investigate and utilize the fundamentals and modulation effect of piezopotential in electronic, optoelectronic, and electrochemical devices by controllably introducing strain and monitoring the change in performance of these devices. We will also extend current understanding/concept of piezotronics/piezo-phototronics, obtained from single-nanowire-based-devices, to functional devices based on large-scale ordered array. The long-term impact of this work will be to develop nanowire-based piezotronic/piezo-phototronic devices for sensing, intelligent micro/nano-systems and human-electronics interfacing.

FY 2012 HIGHLIGHTS

We have successfully demonstrated strain-gated piezotronic transistor, of which the transport characteristics can be modulated by external mechanical strain [Adv. Mater. 22, 4711-4715, (2010)]; strain-modulated piezotronic resistive memory, which can record and store the information of applied strain for later access [Nano Lett. 11, 2779-2785, (2011)]; and nanowire-based optoelectronics devices such as solar cells, photodetectors, and LEDs with enhanced performance by piezopotential due to piezo-phototronic effect [Nano Lett. 11, 4812-4817, (2011); ACS Nano 4, 6285-6291, (2010); Nano Lett.

11, 4012-4017, (2011)]. In the next period, we envision investigating piezotronic/piezo-phototronic effect in electronic, optoelectronic, and electrochemical devices as well as array-based devices and implement large-scale array piezotronic/piezo-phototronic systems.

Measurement of Near-Field Thermal Radiation between Flat Surfaces with a Nanogap

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Funding:	$100,000

PROGRAM SCOPE

Evanescent waves and photon tunneling are responsible for the predicted near-field energy transfer being several orders of magnitude greater than that between two blackbodies, i.e., breaking Planck's law. The enhanced energy transfer may be used for improving the performance of energy conversion devices, augmenting laser cooling, developing novel nanothermal manufacturing techniques, and imaging structures with high spatial resolutions. The method proposed here is to use ultrasmall gaps for measuring nanoscale radiation between flat surfaces with an area as large as 1 cm^2. This will yield the first quantitative demonstration of near-field radiation between relatively large flat surfaces down to 20 nm distance and thus will be a huge step toward practical realization of near-field thermophotovoltaic devices. A fundamental challenge exists as whether or not the predicted nanoscale radiation theory violates the second law of thermodynamics. By introducing entropy density and entropy flux concepts to near-field radiation analysis, this project attempts to offer a second law justification of near-field thermal radiation, especially with surface plasmon or surface phonon polaritons. This study is well aligned with the PI's long-term goals of providing leadership and expertise in thermal radiation at the nanoscale for energy harvesting as well as of educating students and future leaders in this area. Both fundamental advancement and experimental breakthrough are expected to result from this project. The effect of nanostructures on the thermal radiative properties will be investigated from both the near-field and far-field considerations.

FY 2012 HIGHLIGHTS

We have considered various options of fabrication of nanogaps over large areas and designed a facility for measurements of the thermal resistances across nanogaps. The designed structures are currently being fabricated, and the thermal measurement facility is being developed. We have studied a number of materials such as doped SiGe alloys, doped Si, metals and dielectrics for controlling near-field thermal radiation, and envisioned a vacuum rectifier concept. We have also performed a study of the energy streamlines during photon tunneling in near-field thermal radiation. We have theoretically validated a generalized Kirchhoff's law for layered structures with a nonuniform temperature distribution. We have experimentally measured coherence thermal emission from an asymmetric Fabry-Perot cavity structure up to 800 K. An effort has been developed to investigate nanostructures (including vertically aligned carbon nanotubes, obliquely aligned Ag nanorods, as well as periodic metamaterials) for the control of thermal radiative properties particularly in the infrared region.

Amorphous Structure and Polymorphs of the Phase-Change $Ge_2Sb_2Te_5$ Chagolgenide Glass

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Funding: $150,000

PROGRAM SCOPE

Phase-change multi-component chalcogenide materials, with $Ge_2Sb_2Te_5$ (GST) as a prototype alloy, are of strong interest because they are used as the media for high-density rewritable data storage. The amorphous (*a*-GST) and crystalline (*c*-GST) states possess significantly different optical and electronic properties. At the same time, GST can be rapidly switched between the two states (the crystallization of the *a*-GST happens on the time scale of several nanoseconds). Such characteristics are ideally suited for applications not only in rewritable optical data storage (CDs and DVDs), but also in electronic phase-change memory. The latter is a non-volatile memory that has fast data transfer rates and high storage densities, with the potential to replace flash memory in the future.

The desirable behaviors of GST must originate from the internal atomic structures of the amorphous and crystalline phases, as well as the unique chemical bonding features in these two states. Presumably, the reversible transformation between the *a*-GST and the *c*-GST only involves easy atomic rearrangements, such that the phase change process can be ultra-fast, while the changes in the chemical bonding are sufficient to produce a large contrast in optical and electronic properties. A thorough understanding of the atomic structure, chemical bonding, possible competing phases, phase relations, and actual phase selections in transforming *a*-GST is highly important to the science of phase-change materials. The new phases and structural variations offer the room for controlling and optimizing the properties of GST materials, and are thus relevant to future development for their broadened data storage applications.

This proposal builds on our recent success and experience in uncovering the atomic-level structure and poly(a)morphism, but shifts the emphasis from metallic glasses to GST. We will continue to take advantage of our two-pronged experimental/computational approach, employing synchrotron (in situ) experiments and ab-initio molecular-dynamics calculations. Our goals are three-fold. The first is to understand the atomic structure and the chemical bonding in the GST glass; a comparison with those of the *c*-GST is expected to explain the ultra-fast (crystallization) switch speed and the large property contrast between the two phases. The second goal is to map out the phase relationships in the pressure (P)-temperature (T) space for GST. The crystalline polymorphs at the 2-2-5 composition, including new metastable phases, will be discovered and identified to shed light on the phase transformation sequence, and expand the realm of possibilities for the GST properties. The third goal is to discover and understand the polyamorphic transitions between different *amorphous* states of the GST glass. While the alloy remains amorphous, the atomic packing and electronic structures will become different in these different polyamorphs. We will explore the property changes associated with the different densities and electronic structures.

Electron Dynamics in Nanostructures in Strong Laser Fields

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Funding:	$150,000

PROGRAM SCOPE

This project aims to investigate novel physical effects in nanomaterials in strong laser fields. The laser fields will be strong enough to pull out and accelerate electrons from the nanoparticles and to transiently modify the material's electronic properties. The project aims to advance the fundamental understanding of how the collective electron motion in strong laser fields is established, how its precise evolution depends on the driving light waveform, how the material properties are influenced by the strong field, and over which pathways and timescales the collective motion decays. The laser-driven collective electron dynamics can unfold on attosecond time scales (one attosecond is a billionth of a billionth of a second) and will be traced by employing attosecond nanoplasmonic streaking spectroscopy. The studies will focus on isolated dielectric, semiconductor and metal nanoparticles. The project can uncover new functionalities of nanomaterials and enable transformative photonic applications of nanostructured devices for the development of sustainable energy sources and ultrafast information and computation technology.

FY 2012 HIGHLIGHTS

We have conducted experiments on the phase-resolved acceleration of electrons near large dielectric nanoparticles. The measured asymmetric electron momentum distributions are currently being theoretically modeled. We also designed a novel high-energy velocity-map imaging spectrometer, which is currently being built and will serve to measure emitted electrons at higher intensities, where non-linear effects play a larger role. Efforts towards the implementation of attosecond nanoplasmonic streaking from nanostructures are underway. Our very first results in this direction were the generation of sub-4 fs pulses and the generation of high-order harmonics using a new 10 kHz laser system, which was installed in July 2012.

Electric Field Effects in Liquid Crystals with Dielectric Dispersion

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Funding:	$180,000

A summary for this program was not available at press time.

Diblock Copolymer Templated Inorganic Nano-Composites

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Funding: $163,000

PROGRAM SCOPE

Our goals are to achieve room temperature magnetoelectrics (MEs) and understand excitonic magnetism. The renaissance of the field of MEs, which started around the beginning of the last decade, has to date yielded a much deeper understanding of the subject of single phase and composite magnetoelectrics. So far, most attention was devoted to inorganic crystalline magnetoelectrics. Here, asymmetric charge ordering in transition metal compounds gives rise to Type-I magnetoelectricity in $LuFe_2O_4$ and crystalline $(TMTTF)_2X$. Type-II magnetoelectrics can be formed by charges created by non-centrosymmetric spin density waves. In general, magnetoelectric order occurs in systems where the kinetic energy of the interacting electrons is smaller than the magnetoelectric potential. Therefore, the Curie temperatures of all known magnetoelectrics fall below room temperature. A similar restriction does not apply for excitonic ferromagnets; therefore, room temperature excitonic ferromagnets and even excitonic magnetoelectrics should exist.

FY 2012 HIGHLIGHTS

The two PIs have jointly published two papers [Advanced Materials 24, 724, (2012); Advanced Materials DOI:10.1002/adma.201204113 (2012)]. The first on organic exciton multiferroics describes the magnetization of single crystal nanowire P3HT doped with PCBM changes under illumination with visible light, electric field, and mechanical stress. The magnetoelectric coupling effect is of the order of 40 mV/cm Oe at a bias magnetic field of 100 Oe. Illumination of the composite with 615 nm light increases the magnetization about two fold; and the stress dependence of the magnetization is characterized by $\frac{\partial M}{\partial \sigma}\big|_{H,T} \approx 4 \cdot 10^{-6}\ \mathrm{Oe}^{-1}$, significantly larger than that of crystalline metallic ferromagnets. Thus, nw-P3HT/PCBM, a robust room temperature organic exciton multiferroic, is a material where polarization, magnetism, light and mechanical distortion all interact. Exciton multiferroics possess four degrees of freedom that could potentially couple to multifunctional nanodevices.

The second paper reports the synthesis of block polythiophenes with crystallinity contrast and distinct electronic properties demonstrating the potential of this mode of morphology control toward new organic exciton multiferroics. The polymers are synthesized using the Quasi-living GRIM method and feature an intrinsic band offset between the two blocks as confirmed by fluorescence spectra and cyclic voltametry measurements. The bicontinuous network formed within two distinct electronic blocks will facilitate high charge separation yielding efficient charge transport and excitonic magnetism. AFM-based images reveal microphase separated block copolymer thin films with distinct magnetic domain structures. A large ME coupling coefficient of 79.6 mV Oe-1cm-1 of the 3:1 ratio P3HT-b-P3HCT thin film sample is observed under an electric field of $4*10^{-2}$ $MVcm^{-1}$ and 100 Oe bias magnetic field.

Electrochemically-Driven Phase Transitions in Battery Storage Compounds

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Funding:	$196,000

PROGRAM SCOPE

Compounds of interest for ion storage in advanced batteries frequently exhibit phase transformations, driven by large and variable electrochemical driving forces inherent to practical use. A combined theoretical-experimental study carried out by MIT and Lawrence Livermore National Laboratory will develop a predictive understanding of the interaction between materials variables such as composition and associated transformation strains, crystallite size and shape, especially at the nanoscale, and electrochemical conditions driving the phase transition, especially the electrical overpotential and its time evolution. Model systems of fundamental and practical interest to be studied include lithium transition metal olivines, $\mathrm{Li}M\mathrm{PO_4}$ (M = Fe, Mn, + additives), and oxide spinels, $\mathrm{LiNi_{0.5}Mn_{1.5}O_4}$, and $\mathrm{Li_4Ti_5O_{12}}$. Phase-field modeling of phase stability and transformation pathways is combined with in-situ experiments in which electrochemical titration is conducted simultaneously with characterization by synchrotron x-ray diffraction, neutron scattering, and transmission electron microscopy, using DOE facilities. The ability to control phase transformation pathways is expected to lead to new materials design concepts that improve battery performance in categories such as the utilization of active materials at high charge/discharge rates, voltage and capacity hysteresis, and cycling-induced mechanical fatigue affecting life.

FY 2012 HIGHLIGHTS

During FY 2012, neutron scattering experiments were initiated, complementing ongoing in-situ synchrotron x-ray diffraction studies. For sensitivity to Li position not possible in the x-ray experiments, a new series of experimental materials was synthesized using $^7\mathrm{Li_2CO_3}$ as a precursor. Powders varying systematically in crystallite size from ~40nm upwards in $^7\mathrm{LiFePO_4}$ and $^7\mathrm{LiMn_{0.4}Fe_{0.6}PO_4}$ were prepared. Neutron scattering experiments have been scheduled at ORNL and LANL, with the first experiment being at the latter and scheduled for Dec 2012. In-situ synchrotron x-ray diffraction studies of the same materials are scheduled at BNL in November 2012 and at APS in March 2013. In the olivines, a central question to be answered is the identity of the x-ray amorphous metastable phase formed during electrochemical cycling of nanoscale crystallites. Initial results from laboratory-synthesized and commercially produced nanoscale olivines (e.g., from commercial cylindrical cells) show that the metastable phase constitutes up to 50% of the electrode-active material when at intermediate states of charge and also that the metastable phase crystallizes to the equilibrium endmember phases over about 1h at room temperature. Thus the metastable phase persists over a time scale relevant to practical duty cycles in applications such as electric vehicles.

First Principles Determination of Structure, Thermodynamics, and Transport in Metals and Oxides

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Funding:	$173,000

A summary for this program was not available at press time.

Near-Field Thermal Radiation at Extreme Separations

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PROGRAM SCOPE

This project aims to investigate, both experimentally and theoretically, heat transfer between two closely spaced objects, focusing on separation between the two surfaces from physical contact to tens of nanometers. The PI has succeeded in the past measuring near-field radiation heat transfer between a sphere and a flat plate using a bi-layer atomic force microscope cantilever, and demonstrated that near-field radiation heat transfer can be several orders of magnitude higher than the predictions of the Planck blackbody radiation law when the two surfaces are separated by tens of nanometers. In this project, the technique will be further improved and used to carry out systematic investigations of heat transfer between two surfaces at extremely close separations, from physical contact to tens of nanometer range. Such experiments will reveal interest phenomena when heat transfer transitions from conduction to radiation. Experimental studies will be accompanied by theoretical investigations.

FY 2012 HIGHLIGHTS

Progress was made in both experimental and theoretical aspects of near-field radiation heat transfer. In the experimental area, the PI continued near-field experiments on near-field heat transfer between two surfaces, addressing issues of surface roughness by developing techniques to smoothen glass spheres. Near-field radiation heat transfer between two metallic surfaces showed smaller enhancements compared to between two glass surfaces, consistent with theoretical expectations. The team also successfully developed a fabrication process for the proposed bi-arm cantilevers, and demonstrated that such cantilevers have 10-fold improvements in thermal sensitivity and, at the same time, minimize force effect, compared to commercial cantilevers.

In the theory area, the team developed analytical/numerical methods for computing heat transfer in a variety of set-ups, including a detailed derivation of heat radiation and heat transfer for N arbitrary objects in the framework of fluctuational electrodynamics in thermal non-equilibrium. Several analytical, asymptotic laws for heat transfer were developed, which might provide additional understanding and checks of experimental results. These efforts enabled effective computation of the near-field radiative transfer for the sphere-plate set-up, mimicking precisely the experimental situation. The team also developed a framework to treat nonlocal effects when two surfaces come to near contact, and is finalizing codes to obtain numerical results.

Surface Engineering by Simultaneous Action of Multiple External Fields

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Funding:	$245,000

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 (metallic, such as Cu) and semiconducting (such as Si) solids under the simultaneous application of mechanical stresses, electric fields, and temperature gradients. We emphasize identifying the conditions under which the multiply-driven surface morphology is stable and exploring the complexity of the corresponding various morphologically stable surface patterns. We also emphasize the driven evolution of nanoscale features aiming at stabilizing and controlling nanoscale patterns on surfaces by their manipulation through simultaneously applied multiple external forces. Specifically, we address systematically 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 islands grown epitaxially on substrate surfaces. The research is based on a modeling approach that combines theoretical analyses of surface morphological stability with self-consistent dynamical simulations of driven surface evolution based on properly parameterized continuum and multi-scale surface transport models.

FY 2012 HIGHLIGHTS

(1) We have developed a three-dimensional model that explores the effects of substrate engineering on the electromigration-driven surface morphological stabilization of epitaxial thin films against Stranski-Krastanow instabilities. We have demonstrated that the use of finite-thickness compliant substrates can reduce the critical electric-field requirement for surface stabilization by ~3 orders of magnitude with respect to that for practically infinitely thick, rigid substrates.

(2) We have developed a fully nonlinear model for the current-driven dynamics of epitaxial (both homoepitaxial and heteroepitaxial) single-layer islands on crystalline substrates. We have validated the model by comparing its predictions of island morphology and size dependence of island migration speed with recently published experimental measurements. We have predicted the driven island morphological evolution and stability as a function of island size and misfit strain.

(3) We have developed a fully nonlinear model that explores synergistic effects of externally applied electric and thermal fields on the surface stabilization of stressed crystalline solids. We have

demonstrated such synergistic effects for surfaces of uniaxially stressed bulk solids. We have extended the model to the analysis of coherently strained epitaxial films on crystalline substrates.

(4) We have analyzed the electromigration-driven complex dynamics of void surfaces in stressed <100>-oriented thin films of face-centered cubic metals under the most general biaxial mechanical loading and mapped the void-surface stability (type and stability of void asymptotic states).

Extreme Thermoelectric Behavior in Low-Dimensional Oxide Conductors

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Funding:	$145,000

PROGRAM SCOPE

This program involves experimental studies of low-dimensional, bulk oxide conductors exhibiting thermoelectric behavior. The investigations are motivated by preliminary research of the PI revealing a giant Nernst effect at low T in quasi-one-dimensional (Q1D) $Li_{0.9}MoO_{17}$ (“Li-purple bronze” or LPB), and very large Seebeck anisotropy near room temperature in both LPB and the Q1D perovskite-related compound, $Sr_5Nb_5O_{17}$. It is argued that the novel characteristics of LPB (Q1D electrons, large Fermi surfaces, bipolarity, low-D phonons, possibly strong electron correlations) make it a model system for investigating the limits of conventional metals physics and the Nernst effect. Studies at room temperature and above are aimed at testing the PI’s hypothesis that extreme Seebeck anisotropy has its origin in interlayer (or interchain) resonant tunneling through defect states (e.g., via energy filtering). Additional studies are proposed to test recent band-structure predictions of extreme Seebeck anisotropy in the delafossite compounds, $PdCoO_2$ and $PtCoO_2$, for which interlayer transport is through coherent band motion.

The physics and physical properties of the materials targeted for study overlap research interests in both the correlated-electron and thermoelectrics communities. The extreme thermoelectric effects being investigated have potential in thermoelectric applications (cooling, power generation, or energy detection). The surprising magnitude of the Nernst coefficient in LPB motivates proposed examination of its potential for application in Ettingshausen cooling. The PI’s thermal conductivity measurements suggest that its thermomagnetic figure of merit might be significantly enhanced through a reduction of the thermal conductivity transverse to its conducting chains. Partial chemical substitution at the Li site by more massive Na, K, or Rb ions is proposed as a means to achieve the desired effect. The thermomagnetic properties of these substituted crystals will be investigated. In addition, these chemical substitutions provide a means to alter the distribution and/or energy of interchain defect states, thereby enabling tests of Seebeck anisotropy hypotheses.

FY 2012 HIGHLIGHTS

As this project began September 15, 2012, work to date has focused on fabrication of a high-temperature probe for Seebeck measurements up to T=600 $^{\circ}$C and the purchase of a new ^{3}He probe and magnet system to extend existing low-T capabilities.

Domain Microstructures and Mechanisms for Large, Reversible and Anhysteretic Strain Behaviors in Phase Transforming Ferroelectric Materials

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Funding:	$126,000

PROGRAM SCOPE

The goal of this project is to perform a theoretical and computational investigation of some fundamental principles and mechanisms and their synergistic operations for achieving advanced strain behaviors in phase transforming ferroelectric materials. The proposed research focuses on the newly discovered, previously unexplored perspectives of domain size effects, domain wall behaviors, nanodomain microstructures, and coherent scattering and interference effects peculiar to nanodomain diffraction in the technologically important perovskite-type ferroelectrics. The project aims to advance the fundamental understanding of field-induced strain behaviors to achieve a desired combination of advanced attributes of large, reversible, and anhysteretic strains (these strain attributes usually compromise each other, leading to trade-offs that seriously limit material's applicability to electromechanical sensors, actuators, and transducers). Six thermodynamic and kinetic principles and mechanisms will be systematically investigated and synergistically integrated: (1) field-induced inter-ferroelectric structural phase transformation to achieve large strain, (2) field-induced stable-metastable phase transformation to maximize reversibility, (3) heterogeneous nucleation-and-growth process at domain walls to enhance low-field responses, (4) domain wall broadening mechanism and domain size effect to exploit nanoscale engineered domain microstructures, (5) deactivation of domain wall motion by applying external fields along nonpolar axes to minimize hysteresis, and (6) bridging domain mechanism and phase coexistence to promote ferroelectric shape memory effects. The project will develop phase field approach-based computational tools and perform simulation studies of domain microstructures and mechanisms for achieving advanced strain behaviors in ferroelectric materials, and develop a new nanodomain diffraction theory to analyze diffraction data, identify nanoscale domain microstructures and mechanisms from diffraction experiments, and correlate computations and experiments.

FY 2012 HIGHLIGHTS

We have investigated mechanisms of nucleation and growth of domains during ferroelectric phase transformation, studied effects of grain textures and shapes on piezoelectric properties of ferroelectric polycrystals, developed diffraction theory of diffuse scattering for heterogeneous displacements and strains in nanodomained crystals, and related diffuse scattering phenomenon to phonon softening behavior. Further investigation focuses on grain texturing of templated grain growth and composite effects on textured ferroelectric ceramics.

Exploring Electric Polarization Mechanisms in Multiferroic Oxides

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Funding:	$165,000

PROGRAM SCOPE

This proposal focuses on understanding the mechanisms involved in the onset of high temperature ferroelectricity in hexagonal $RMnO_3$ and at low temperature in E-Type magnetically ordered perovskite $RMnO_3$. We are synthesizing preovskite small A site multiferroics by high pressure and high temperature methods. The orthorhombic phase will also be obtained by thin film deposition on YSZ substrates. 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 and magnetic ordering will be probed with temperature and pressure dependent far infrared absorption and Raman spectroscopy. The orthorhombic system (small radius R ions), which is believed to exhibit electronically driven ferroelectricity, will also be examined. The experimental work will be complemented by density functional methods to determine the magnetic ground states and *ab initio* molecular dynamics methods to determine the high temperature structures.

FY 2012 HIGHLIGHTS

Atomic and electronic structure measurements combined with *ab initio* molecular dynamics simulations provide a new picture of the origin of ferroelectiricity in hexagonal $RMnO_3$ multiferroics. Unlike the (Ti) off-centered titanates, with respect to the Mn sites, we find no large changes in bond distances, thermal factors, hybridization or electronic structure in the ferroelectric phase (below T_{FE}~875K). The Born effective charge tensor is found to be highly anisotropic at the O sites, indicating very strong hybridization, and does not change significantly above T_{FE}. At the R site, however, a reduction of the average local R-O bond with increased temperature is found. *Ab initio* molecular dynamics calculations on $HoMnO_3$ reveal large displacements of the Ho, O3 and O4 ions along the z-axis which reduce the buckling of the MnO3/O4 planes above T_{FE}. The changes result in O3/O4 ions moving to central points between z-axis pairs of Ho ions. These structural changes make the R sites more symmetric thus extinguishing the electric polarization. At higher temperatures, rotation of MnO_5 polyhedra occurs without much change in polarization.

Crystal structure, electric polarization, and heat capacity measurements on the hexagonal Multiferroic $RMnO_3$ reveal that small R ion (Lu and lower cation size) systems are ferroelectric and possess the same space-group as YMnO3. Combined local and long-range structural measurements were conducted by XAFS, PDF, and single crystal and powder XRD methods. The precise structural features in the R-O distribution which optimized the electrical polarization have been explored. Samples which have higher electric polarization than the classical $YMnO_3$ system have been synthesized and studied. The new materials will lead to devices with enhanced data storage capacity.

Structure and Magnetism in Novel Group IV Element-Based Magnetic Materials

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Funding: $0.00 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

The project is to investigate structure, magnetism, and spin-dependent states of novel group IV element-based magnetic thin films and heterostructures as a function of composition and epitaxial constraints. The materials systems of interest are Si-compatible epitaxial films and heterostructures of Si/Ge-based magnetic ternary alloys grown by non-equilibrium molecular beam epitaxy (MBE) techniques, specifically doped magnetic semiconductors (DMS) and half-metallic Heusler alloys. Systematic structural, chemical, magnetic, and electrical measurements are carried out using x-ray microbeam techniques, magnetotunneling spectroscopy and microscopy, and magnetotransport. The work is aimed at (1) elucidating the nature and interplay between structure, chemical order, magnetism, and spin-dependent states in these novel materials; (2) developing materials and techniques to realize and control fully spin polarized states; and (3) exploring fundamental processes that stabilize the epitaxial magnetic nanostructures and control the electronic and magnetic states in these complex materials. A combinatorial approach provides the means for the systematic studies, and the complex nature of the work necessitates this approach.

FY 2012 HIGHLIGHTS

We have grown binary and ternary composition spread epitaxial films of $Co_xMn_ySi_z$ in (111) and (001) orientations. We have determined that the highest structural and chemical ordering occurs at compositions away from the Heusler stoichiometry of Co_2MnSi. Processes for making arrays of tunnel junctions on combinatorial composition spread samples have been developed, which involve in-situ deposition of high quality ultra thin films of aluminum oxide and superconducting Nb and processing individually addressable junctions. In the next period, we plan to carry out systematic spin dependent tunneling spectroscopy measurements to investigate spin dependent states and polarization as a function of composition and correlate them with structural and chemical ordering.

Bridging Atomistic and Continuum Scales in Phase-Field Modeling of Stressed Polycrystalline Materials

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Funding:	$146,000

PROGRAM SCOPE

This research seeks to develop state-of-the-art and scale-bridging phase-field methodologies to understand the physical behavior of stressed polycrystalline materials with particular focus on high homologous temperature and solute effects. Phase-field simulations are aimed at elucidating equilibrium structures of hot grain boundaries and fundamental mechanisms of stress-driven grain boundary motion in the high-dimensional parameter space of grain boundary. This research takes advantage of the unprecedented opportunity to tackle those complex phenomena based on a wealth of new observations from in situ imaging studies of internal material interfaces together with recent advances in atomistic and continuum simulations. Conventional phase-field and phase-field-crystal simulations are combined with molecular dynamics simulations in order to bridge quantitatively atomistic and continuum length and time scales. Multiscale modeling is expected to contribute new scientific understanding of interfacial processes relevant for the improved performance, design, and safety of manufactured structural and electronic materials for diverse energy-related applications.

FY 2012 HIGHLIGHTS

We have derived new fundamental relations between the equilibrium thermal fluctuation spectrum of a grain boundary and the coupling factor that characterizes its normal motion driven by shear deformation outside of equilibrium [A. Karma, Z.T. Trautt, and Y. Mishin, *Phys. Rev. Lett.* 109, 095501 (2012)]. These results shed light on the relationship between grain boundary fluctuation and motion coupled to shear deformation. Furthermore, they establish a new computational methodology for extracting basic GB properties to model microstructural evolution. We have used linear stability theory and phase-field simulations to show that spontaneous phase separation in elastically coherent solids is fundamentally altered by the presence of free surfaces [M. Tang and A. Karma, *Phys. Rev. Lett.* 108, 265701 (2012)]. Due to misfit stress relaxation near surfaces, phase separation is mediated by unique surface modes of spinodal decomposition. Those modes have faster kinetics than bulk modes and are unstable even when spinodal decomposition is suppressed in the bulk. Consequently, in the presence of free surfaces, the limit of metastability of supersaturated solid solutions of crystalline materials is shifted from the coherent to chemical spinodal. We expect those novel surface modes of coherent spinodal decomposition uncovered in this study to be an especially important phenomenon in nanostructures, in which the surface area to volume ratio is very high and bulk spinodal decomposition may even be suppressed.

Intensive Variables and Nanostructuring in Magnetostructural Materials

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Funding:	$90,000

PROGRAM SCOPE

The programs seeks to understand, predict, and ultimately tailor magnetostructural transitions for potential energy-relevant applications. To this end, the effects of extrinsic parameter variation, detailed composition, and microstructural scale on magnetostructural 1st-order phase transitions in equiatomic FeRh and MnBi are investigated.

FY 2012 HIGHLIGHTS

Studies have primarily focused on (1) understanding the effects of nanostructuring on the magnetostructural response in FeRh, augmented by preliminary work on the MnBi system, and (2) clarifying predictive trends concerning the relationship between alloying element substitution and magnetostructural transition temperature in equiatomic FeRh.

The equiatomic CsCl-structured (B2-type) FeRh was nanostructured via two main approaches: (1) heat-treatment of a rapidly solidified precursor alloy of composition, $Cu_{95}(FeRh)_5$, and (2) post-deposition processing of FeRh thin films deposited on Cu and Al_2O_3 matrices.

Advanced characterization was carried out using TEM and electron diffraction (collaboration with Prof. J. E. Shield, U. Nebraska) and with transmission x-ray diffraction Beamline X16C at the National Synchrotron Light Source at Brookhaven National Laboratory. FeRh nanoprecipitates of ~ 8 nm diameter are confirmed to consist of the AuCu-I ($L1_0$)-type structure that transitions to the expected CsCl-structured (B2-type) structure with annealing-induced grain growth, highlighting potential for tailoring magnetostructural transitions in functional materials systems via nanostructuring. Clarification of the role of elemental substitutions on the FeRh magnetostructural transition was successfully achieved with a phenomenological model that categorizes the influence of alloying additions 3*d*, 4*d* and 5*d* character on the FeRh magnetostructural transition, as reported in the literature since 1964. This significant achievement adds predictive capability to a decades-old problem and allows predictive insight into this intriguing phase transition.

Functional Imaging of Hybrid Nanostructures: Visualization of Mechanisms for Solar Energy Utilization

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Funding:	$140,000

PROGRAM SCOPE

The project utilizes Raman scattering, multi-wavelength optical excitation, and electrical transport measurements of nanowire-based hybrid materials structures to resolve, in energy and space, the absorption of light, the generation of excess energetic charge carriers, and the efficiency of their separation to generate electrical and chemical energy. The overall project goal is to isolate and quantify various steps in the energy conversion process, including geometrically and plasmonically enhanced absorption, the generation of carriers with excess energy, and the efficiency with which the carriers can move to and perform useful chemistry at interfaces. Single nanostructure measurements on model nanowire hybrid systems are being extended to liquid environments and ensemble measurements to establish relationships between nanostructure, electronic structure, and photoelectrical and photoelectrochemical activity.

FY 2012 HIGHLIGHTS

Semiconducting nanowires are promising light-harvesting units with enhanced absorption compared to bulk films of equivalent volume. A quantitative account of nanowire absorption is therefore a foundation for engineering advanced photovoltaic and photo-electrochemical devices. Single crystal tapered silicon nanowires were grown to reveal multiple electromagnetic resonances that induce broad-band light absorption and scattering. The diameter-dependent Raman scattering intensities, which depend on the fourth power of the electromagnetic field, were quantitatively matched with model calculations using finite-difference time-domain techniques, providing a stringent test of the model. These studies benchmark the potential for numerical models to describe absorption in semiconductor nanostructures, supporting their use in the design of optimal light harvesting systems.

While the efficacy of absorption is described by the external quantum efficiency, the internal quantum efficiency depends on the ease of transport within materials and across interfaces. We have developed methods to perform internal photoemission measurements at high spatial resolution and have demonstrated the quantification of energy barrier heights at metal semiconductor interfaces. These interfaces are important for efficiently extracting charge from photovoltaic devices and for photo-electrochemical conversion in approaches that utilize co-catalysts.

High Performance Nano-Crystalline Oxide Fuel Cell Materials: Defects, Structures, Interfaces, Transport, and Electrochemistry

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Funding:	\$500,000

PROGRAM SCOPE

This project focuses on solid oxide cells (SOCs)—versatile electrochemical devices with applications including clean efficient electricity generation, chemical production, renewable fuel production, and electricity storage. Solid oxide fuel cells, arguably the most important and most developed application, are nearing commercial viability, but fundamental challenges remain, especially reducing operating temperature and improving long-term durability. Operating temperature is important not only for making the technology more viable, but for enabling new uses such as transportation and portable generation.

This project aims to utilize nano-scale materials to address electrode performance and durability issues that currently limit SOCs. The research encompasses air electrodes, fuel electrode, and electrolyte materials. The scientific focus is on understanding the enhanced electronic and ionic transport properties of mixed nano- and micron-scale oxide structures, and how they impact reduced temperature electrochemical processes. Novel methods for forming highly functional nano-structures are being developed. Detailed investigations of the transport and electrochemical properties of various important oxygen ion conductor and mixed ion and electronic conductor (MIEC) materials, in nano-crystalline form, are being carried out using novel analysis methods. Computational efforts are focusing on elucidating the factors impacting long-term materials stability in both fuel cell and electrolysis modes.

FY 2012 HIGHLIGHTS

The electrochemical performance and stability of air electrodes with $(Sm,Sr)CoO_3$ (SSC) wet-impregnated into Gd-doped Ceria or doped Lanthanum Gallate scaffolds have been studied. The nano-scale structure provides low polarization resistance values down to 500^oC, much better than conventional electrodes. However, the stability of the nano-structures is still in question even at this reduced operation temperature; our recent stability studies have illustrated the importance of the details of the nano-structure, where it is critical to avoid SSC particles becoming electrically isolated from each other. Regarding fuel-side electrodes, we have shown that Pd exsolves from oxides under certain conditions, forming Pd nano-particles that greatly enhance the fuel oxidation process and thereby reduce resistance. Interestingly, the Pd particle size decreases with decreasing operating temperature, allowing the electrodes to “adapt” to the lower temperature and yield good performance.

These nano-materials have been implemented in novel reduced-temperature SOCs that yielded the highest power density values ever reported, e.g., > 1 W/cm^2 at 550^oC.

Fabricating Highly Efficient Photocathodes for p-type Dye-Sensitized Solar Cells

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Funding:	$174,000

PROGRAM SCOPE

The objective of this proposal is to fabricate highly efficient photocathode dye-sensitized solar cells (p-DSCs) through the design of new sensitizers and the introduction of new nanostructured p-type semiconductors. The ultimate goal is to integrate these efficient p-DSCs with the well-developed dye-sensitized n-TiO_2 photoanode (n-DSC) to form tandem DSCs. The advantage of a tandem DSC over a single-absorber n-DSC is the capability to achieve more efficient light absorption, since both the anode and the cathode in a tandem DSC are photoactive, while only the anode is photoactive in a n-DSC.

This project has three aspects of activities: (1) designing new dye sensitizers; (2) synthesizing new nanostructured p-type semiconductors with proper valence band (VB) position, high visible transparency, and high hole mobility; and (3) investigating the device physics of the solar cells.

FY 2012 HIGHLIGHTS

We have synthesized a series of cyclometalated ruthenium complexes represented as $Ru[(N^\wedge N)_2(C^\wedge N)]^+$, where N^N represents 2,2'- bipyridine and C^N represents bidentate phenylpyridine derivatives. Our works are the first application of these sensitizers for p-DSCs. These cells show large absorbed photon-to-current conversion efficiencies. We have also reported the first application of delafossite $CuGaO_2$ nanoplates for p-DSSCs and demonstrated the high photovoltages. We have measured the dependence of V_{oc} on the illumination intensity to estimate the maximum obtainable V_{oc} from the $CuGaO_2$-based p-DSSCs. Excitingly, a saturation photovoltage of 464 mV has been observed when a polypyridyl $Co^{2+/3+}$(dtb-bpy) electrolyte was used. Under 1 Sun AM 1.5 illumination, a V_{oc} of 357mV has been achieved. These are among the highest values that have been reported for p-DSSCs.

Nanocrystal-Based Dyads for Solar to Electric Energy Conversion

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Funding: $260,000

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. Because their synthesis and individual properties have been well studied, we have selected CdSe/CdTe as the bandgap-staggered (Type II) nanoparticle composites that we would explore first. Although synthetic control over their size (and somewhat their shape) is well developed, the manipulation of their ligand coatings and their self-assembly into functional structures remain open questions and are a particular focus of our current studies.

FY 2012 HIGHLIGHTS

Our efforts in the past year have focused on three major thrusts: using ligand groups to control/manipulate NP energetics, extending this control of energetics to the control of NP to NP charge transfer, and developing our understanding of NP-electrode Fermi level pinning.

(1) Predicting and Controlling NP Energetics –

- *Computational Studies:* We have performed the first systematic DFT (B3LYP/Lanl2dz) studies of the structural and electronic properties of Cd_nSe_n/Cd_nTe_n nanoparticles ($n = 6, 9$), both bare and capped with amino, thio, or phosphine oxide ligands.
- *Experimental Studies:* We have quantified the electronic energy level positions for assemblies of CdSe NPs and CdTe NPs on a dithiol coated Au electrodes.

(2) Predicting and Controlling NP-NP Charge Transfer – We used our control over the energy level alignment to show how an organized energy level structure affects the charge transfer efficiency in electrochemical systems and in solid-state photovoltaic devices. We have manipulated the energy level alignment by manipulation of the size and surface ligands of the CdTe and CdSe NPs and combined this capability with control over the NPs spatial arrangement.

(3) Fermi Level Pinning – We are exploring the generality of the Fermi level pinning effect for the nanoparticle assemblies and learning how to manipulate it through chemical means.

- *Experimental Studies:* In addition to our detailed studies of Fermi level pinning for CdSe/Au and CdTe/Au assemblies, we have reported Fermi level pinning for CdSe/TiO_2 assemblies.

- *Computational Studies:* The mechanisms of HOMO energy pinning are different in the theoretical and experimental studies, and we are extending our studies of both HOMO/LUMO energy alignment and HOMO pinning to larger species.

Light Trapping, Guiding, and Concentration for Maximizing Solar Energy Conversion

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Funding:	$250,000

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. In conventional silicon thin film solar cells, most of the incident sunlight is either reflected or transmitted. Clearly, thin film architecture is needed to collect and absorb a broad spectrum of sunlight incident from all angles. Another benefit of using thin film architecture is the improved carrier collection efficiency. In this program, we will use three-dimensional photonic crystal to mold the flow of sunlight, to trap and absorb sunlight in an ultra-thin slab of semiconductor material, and to achieve a much improved device performance.

The key challenges for sunlight collection and conversion are to (1) maximize solar trapping and absorption over a broad-θ and $-\lambda$ range, (2) minimize solar reflection over a broad-θ and $-\lambda$ range, (3) improve collection of photo-current, and (4) use less, or an ultrathin slab, of semiconductor material.

Under this program, fundamental innovations are jointly proposed by the P.I. at RPI and by Professor S. John of University of Toronto 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 (400-1200 nm) with an equivalent bulk thickness of one micrometer of silicon. We will also implement a multi-layer graded-index antireflection coating to minimize reflection and to improve the performance of our device. Additionally, we will explore different types of 3D simple cubic photonic crystal that include the layer-by-layer structure and the newly proposed "modulated nano-wire" structure.

A new trend in solar collection and conversion is to bend light by 90-degrees using advanced photonic structures. Under this program, we propose to use a holographic recorded thin film to diffract light by 90-degrees. Our second long term scientific goal is to realize a large-scale holographic thin film that is capable of diffracting a wide spectrum of sunlight by 90-degrees. In doing so, sunlight may be better managed by the well-established planar optics methods to allow a relatively easier guiding, concentration and conversion. The three fundamental innovations that we proposed are (1) the use of volume hologram to achieve 90-degrees bending of sunlight from the sky into a planar film, (2) guiding and concentrating sunlight within the thin film by planar optics, and (3) directing and converting sun light energy into a high efficiency photovoltaic cell. This proposed holographic element is expected to achieve a solar collection of >80% for λ=400-1,200 nm, a solar concentration factor of 10-50 times without the use of any bulky, external mirrors and, hence, greatly reduces the overall cost of a solar panel.

Magnetic Frustration and Cooperative Phenomena in Correlated Electron Oxide Materials

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Funding: $135,000

PROGRAM SCOPE

The goal of this project is to investigate the fundamental physics of magnetism in oxides that exhibit spin frustration either due to structural configuration or unusual phenomena arising from geometry and electron correlation effects. The research has strengthened our continued collaborations with other DOE-funded leading experts and their research groups, including Prof. Sang-Wook Cheong of Rutgers University, Prof. Chris Leighton of the University of Minnesota, and Prof. David Mandrus of the University of Tennessee.

FY 2012 HIGHLIGHTS

By using our developed magnetocaloric and radio-frequency transverse susceptibility techniques, efforts have continued to shed light on the nature of multiphase transitions, phase separation, spin-lattice coupling, and spin frustration in mixed-valent manganites ($La_{5/8-y}Pr_yCa_{3/8}MnO_3$, $Pr_{0.5}Sr_{0.5}MnO_3$, $La_{0.7-x}Pr_xSr_{0.3}MnO_3$, $Sm_{1-x}Sr_xMnO_3$, $La_{0.7}Ca_{0.3}Mn_{1-x}Fe_xO_3$) and cobaltites ($Pr_{1-x}Sr_xCoO_3$), spinel compounds ($Co_{1-x}Ni_xAl_2O_4$), and low-dimensional $Ca_3Co_2O_6$ single crystals. In addition to these, we have been successful with the synthesis and characterization of a large class of nanoscale complex manganites, including $La_{5/8-y}Pr_yCa_{3/8}MnO_3$, $La_{0.4}Ca_{0.6}MnO_{3+\delta}$, and $LaMnO_{3+\delta}$ nanoparticles and $La_{0.5}Sr_{0.5}MnO_3$ nanowires. For instance, $La_{5/8-y}Pr_yCa_{3/8}MnO_3$ (LPCMO) is a unique example of *microscale* phase-separated materials, with coexisting charge-ordered antiferromagnetic (CO/AFM), charge disordered paramagnetic (PM), and ferromagnetic (FM) phases. In contrast to a *nanoscale* phase-separated system, we demonstrate that reducing particle size to the nanoscale, below the microscale phase separation length of CO, has a strong impact on the magnetic and magnetocaloric response of a microscale phase-separated system like LPCMO. Decreasing particle size affects the balance of competing phases in LPCMO and narrows the range of fields over which PM, FM, and CO phases coexist. The FM volume fraction increases with size reduction, until CO is suppressed below some critical size, ~100 nm. With size reduction, the saturation magnetization and field sensitivity first increase as long-range CO is inhibited, then decrease as surface effects become increasingly important. The trend that the FM phase is stabilized on the nanoscale is contrasted with the stabilization of the charge-disordered PM phase occurring on the microscale, demonstrating that in terms of the characteristic phase separation length, a few microns and several hundred nanometers represent very different regimes in LPCMO. Our study provides new and important insights into the effects of size reduction on the strain-driven phase separation phenomena in microscale phase-separated manganite systems.

Energy Transport in Graphene

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Funding:	$174,000

PROGRAM SCOPE/HIGHLIGHTS

The objective of this project is to develop a better understanding of phonon transport and coupled electron-phonon transport in graphene. As a two-dimensional (2D) monatomic layer of sp^2 carbon atoms, graphene is a promising material for future-generation energy-efficient electronic devices and thermal management solutions because of its superior charge mobility, mechanical strength, and thermal conductivity.

The specific aims of this project include the following: (1) Clarify whether the flexural vibration modes make an important or negligible contribution to thermal conductivity of graphene. (2) Investigate the effects of inter-layer coupling, substrate interaction, stress, and morphology on phonon transport in suspended and supported single- and few-layer graphene. (3) Characterize the interfacial thermal transport between supported graphene and underlying dielectric, metallic, and polymeric substrates. (4) Evaluate interfacial thermal transport between graphene and its surrounding gas environment. (5) Determine whether or not coupled electron-phonon transport in graphene is highly non-equilibrium as in carbon nanotubes. (6) Reveal the effects of inter-layer coupling, substrate interaction, stress, morphology, and gas environment on electron-phonon coupling in graphene.

Since the successful exfoliation of graphene from graphite onto a dielectric substrate in 2004, the worldwide research activities on graphene have increased very rapidly. However, despite extensive investigations of electron transport in graphene, there have been few studies of phonon transport and coupled electron-phonon transport in graphene. Consequently, the current understanding of energy transport in graphene is still rather primitive. As an important example, based on quantum mechanical calculations of the phonon scattering process, a critical question has been raised recently on the validity of the usual assumption of negligible contribution to the thermal conductivity from the out-of-plane flexural vibration modes in the 2D monatomic sheet. In addition, we have recently discovered experimentally that the thermal conductivity of supported monolayer graphene is lower than the basal plane values of graphite. Our results suggest the need of better understanding of the important roles of substrate interaction, inter-layer coupling, stress and morphology in phonon transport in graphene. Moreover, while a recent study suggested small interface thermal resistance for graphene embedded in silicon dioxide, thermal interface could be rather different for supported graphene where the morphology could be non-conformal to the surface roughness. On the other hand, while the 2D band phonon temperature in current-carrying graphene has been obtained from a recent Raman measurement, it remains a question whether or not electron-phonon transport in current-carrying graphene is highly non-equilibrium with very different temperatures for different phonon branches, which is the case directly observed by our Raman measurement of individual current-carrying carbon nanotubes.

Understanding Compound Phase Transitions in New Heusler Alloy Giant Magnetocaloric Materials: Extension to Multifunctional Materials

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Funding:	$200,000

PROGRAM SCOPE

There are three central goals of this project. The first deals with discovering new near-room-temperature magnetocaloric materials (primarily Mn-based Heusler alloys and other intermetallic compounds) and understanding the physical origins of the complex magnetostructural phase transitions that drive their physical properties. This will be done by selective elemental substitutions (i.e., controllably changing lattice parameters, chemical pressure, electronic structure, etc.) and varying fabrication parameters. Many of these systems simultaneously exhibit more than one enhanced physical property (for example, large magnetocaloric effects and giant magnetoresistance) in the same temperature regime. The second goal of this project deals with exploring these multifunctional materials and understanding the connections between and the origins of their enhanced physical behaviors. Finally, the third major goal deals with performing direct measurements of the magnetocaloric parameters of these materials (i.e., the adiabatic temperature change) and comparing them to those acquired from indirect measurements (usually calculated from magnetization isotherms or field-dependent heat capacity data). The hope is to gain insight into the validity and accuracy of indirect measurements, which are experimentally much more straightforward to employ.

FY 2012 HIGHLIGHTS

We have found many new giant magnetocaloric effect materials (e.g., $MnNiGe_{1-x}Al_x$) and elucidated the role of Ni-Mn hybridization in the enhanced behavior of some related alloys. We have also identified many new multifunctional systems—for example, a Ni-Mn-In alloy that exhibits both normal and inverse magnetocaloric effects as well as large magnetoresistance all at room temperature. Finally, we have carried out a comprehensive set of direct and indirect magnetocaloric measurements on $Ni_{50}Mn_{35}In_{14}B$ and found excellent agreement between the methods. For these types of polycrystalline alloys, we have concluded that indirect and direct measurements of the magnetocaloric parameters are both in agreement and are accurate.

Densely Aligned Graphene Nanoribbon Arrays and Bandgap Engineering

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Funding:	$235,000

PROGRAM SCOPE

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, (2) develop anisotropic etching of grapheme capable of producing GNR edges with atomically smooth edges along the graphitic crystallographic lattice directions, (3) engineer the bandgap of GNRs using uniaxial strain, (4) use Micro-Raman spectroscopy to quantify the uniaxial strain and characterize edge orientations of GNRs, and (5) enable field-effect transistors (FETs) fabricated on strained high-density GNR arrays with high performance to be compared with those of carbon nanotube FETs and silicon FETs.

Overall, this proposed work will involve basic materials science, chemistry, solid state physics, and electrical engineering. An important potential application is high performance GNR FETs as a candidate for future electronics.

Nanophotonics-Enhanced Solar Cells

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Funding:	$270,000

A summary for this program was not available at press time.

Raman Spectroscopic Study of Coupling between Magnetic and Ferroelectric Orders in Nanoscaled Thin Films Superlattices

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Funding:	$122,000

PROGRAM SCOPE

The objective of this project is the enhancement of magnetoelectric coupling in nanoengineered oxide films and heterostructures that are predicted to show strong magnetoelectric coupling via control of oxygen octahedron rotations. The main focuses of the project are the $(BaTiO_3)_n/(CaMnO_3)_n$ short-period superlattices, which have been predicted to exhibit interface-induced giant magnetoelectric coupling. In the $(BaTiO_3)_n/(CaMnO_3)_n$ superlattices, $BaTiO_3$, which is highly resistant to oxygen octahedral rotations and strongly ferroelectric, suppresses the MnO_6 octahedral rotation in $CaMnO_3$, 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 artificial layered material will be grown by laser MBE from separate oxide targets. Targets of BaO, TiO_2, CaO, and MnO_2 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 $(BaTiO_3)_1/(CaMnO_3)_1$ superlattice will be BaO-TiO_2-CaO-MnO_2, which repeats itself. 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.

Optical and Electrical Properties of III-Nitrides and Related Materials

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Funding:	$158,000

PROGRAM SCOPE

Among the members of the III-nitride material system, boron-nitride (BN) is the least studied and understood. Due to its extraordinary physical properties, such as ultra-high bandgap (E_g ~ 6 eV) and chemical stability, negative electron affinity, and a very large thermal neutron (0.025 eV) capture cross section, BN is very promising for applications of deep ultraviolet optoelectronic devices and solid-state neutron detectors to replace ^{3}He gas detectors, which face a serious issue of shortage. Moreover, hexagonal BN (hBN) has a close lattice match to graphene and is the most suitable substrate and dielectric/separation layer for graphene electronics and optoelectronics. Similar to graphene, low dimensional hBN is expected to possess rich new physics. Other potential applications of hBN include super-capacitors and electron emitters. However, our knowledge concerning the semiconducting properties of hBN is very scarce. The goal of this project is to study this newest family member of the III-nitride material system, hBN, and to address issues that have not yet been explored but are expected to profoundly influence our understanding of its fundamental properties and device applications. The research efforts include (1) further development of epitaxial growth processes for achieving wafer-scale high crystalline quality hBN epilayers, (2) investigation of the nature of band structures of different polytypes of hBN predicted by theoretical calculations, and (3) probing of the two-dimensional (2D) optical and electrical properties of hBN.

FY 2012 HIGHLIGHTS

(1) Achieved the synthesis by MOCVD of wafer-scale (2-inch) hBN epitaxial layers with high crystalline quality—reflected by the realization of the narrowest linewidth of x-ray diffraction (*0002*) *rocking curve* (<400 arcsec).

(2) Realized room temperature band edge emissions in hBN with very high emission efficiency. The observed band edge emission efficiency in hBN epilayers is more than two orders of magnitude larger than that in *wurtzite* AlN.

(3) Investigated novel optical properties of hBN resulted from its unique layered structure. We have shown that the large $p \rightarrow p$ transition rate combined with the large joint density of states of electron-hole pairs resulting from the 2D nature of hBN lead to high emission efficiency in hBN (in collaboration with Dr. Su-Huai Wei of NREL).

Energy Transport in Graphene

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Funding:	$150,000

PROGRAM SCOPE

The objective of this proposed research is to develop a better understanding of phonon transport and coupled electron-phonon transport in graphene. As a monatomic layer of sp^2 carbon atoms, graphene is a promising material for future-generation energy-efficient electronic devices and thermal management solutions because of its superior charge mobility, mechanical strength, and thermal conductivity. Building on the results from our previous study of carbon nanotubes and preliminary results on graphene, this project aims to (1) clarify whether the flexural vibration modes make an important or negligible contribution to thermal conductivity of graphene; (2) investigate the effects of inter-layer coupling, substrate interaction, stress and morphology on phonon transport in suspended and supported single- and few-layer graphene; (3) characterize the interfacial thermal transport between supported graphene and underlying dielectric, metallic, and polymeric substrates; (4) evaluate interfacial thermal transport between graphene and its surrounding gas environment; (5) determine whether coupled electron-phonon transport in graphene is highly non-equilibrium as in carbon nanotubes; and (6) reveal the effects of inter-layer coupling, substrate interaction, stress, morphology, and gas environment on electron-phonon coupling in graphene.

FY 2012 HIGHLIGHTS

We have made several fundamental discoveries related to energy transport in graphene and other sp^2 carbon systems. The scientific findings include the following: (1) Ultrathin-graphite foams are found to possess superior thermal conductivity compared to percolated networks of carbon nanostructures because of the elimination of the interface thermal resistance bottleneck in the covalently bonded networks of ultrathin graphite and few-layer graphene building blocks. (2) Low-frequency phonons in multi-layer graphene (MLG) supported on silicon dioxide is scattered by the amorphous support, and this effect impacts phonon transport in MLG layers at a distance of more than 30 atomic layers away from the interface. (3) Because of phonon scattering by polymer residual on the surface, the thermal conductivity of suspended few-layer hexagonal boron nitride (h-BN) increases with increasing layer thickness, and approaches the bulk value at room-temperature when the thickness is increased to about ten layers.

Light Trapping, Absorption, and Solar Energy Harvesting by Artificial Materials

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Funding:	$135,000

PROGRAM SCOPE

The goal of this project is to design and simulate thin-film solar light trapping structures that improve solar cell efficiency beyond current state-of-the-art architectures. A primary focus is on silicon-based solar cells but the same design principles apply to solar cells made of GaAs, organic materials, and dye-sensitized titanium oxide. The new design principle is based on the phenomenon of parallel-to-interface refraction (PIR) of incoming sunlight in which light from a broad range of incoming angles and a wide range of frequencies is deflected into “slow-light” modes that propagate nearly parallel to the interface between the solar cell and air. The photonic crystal provides an enhanced electromagnetic density of states into which sunlight is trapped and has a long dwell time. This long dwell time (associated with optical cavity resonances) enables strong absorption of light even when the intrinsic absorption of the active material (say silicon) is very weak. This project includes detailed simulation of Maxwell’s equations for light propagation and absorption in materials with complex frequency-dependent dielectric function and detailed simulation of the semiconductor drift-diffusion equations for various choices of P-N junction and electrical contact geometries.

FY2012 HIGHLIGHTS

We have completed our optimization of solar light trapping and absorption in nanowire photonic crystals. We have also evaluated the electronic response of solar cells based on nanowires to determine the resulting short circuit current, open circuit voltage, and overall power efficiency. We find that with roughly one micron of (equivalent bulk thickness) silicon, it is possible to absorb 75% of all available sunlight in the wavelength range of 400 nm- 1000 nm, over a broad range of incident angles (0-60 degrees) relative to normal incidence. This implies that, with a much smaller amount of silicon, namely one micron, it is possible to achieve greater solar absorption than in conventional designs where 50-300 microns of silicon is utilized. Using a radial P-N junction geometry in our modulated silicon solar nanowires, we obtain a short circuit current of nearly 28 mA/cm2 and an open circuit voltage of 0.62 Volts. In the case of conical pore photonic crystals, we find, with only one micron of silicon and optimization of the shape and orientation of the nano-pore, a maximum achievable photo-current density (MAPD) of 36 mA/cm2 in the absence of SiO2 packaging and a reduced MAPD of 33 mA/cm2 in the presence of SiO2 packaging. The former result corresponds to the absorption of 85% of all available sunlight in the range of 350-1100 nm, using only one micron of silicon. This is the highest level of light trapping and absorption ever reported (to our knowledge) for one micron of silicon. Overall power conversion efficiencies are in the range of 15-20%. In future work, we aim to include nonlinear optical effects that compress the solar spectrum through optical up-conversion and down-conversion effects to further improve these efficiencies.

Coherent Control of Spin States in Organic Electronics

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Funding:	$0.00 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

This project focuses on the investigation of spin-dependent electronic transitions in organic semiconductors. These materials are used for lighting and photovoltaic applications. The spin degree of freedom (which is connected to the magnetic degree of freedom) of charge carriers is known to greatly influence electronic processes in organic semiconductors and, in particular, the efficiency of devices. Understanding spin-dependent processes and illuminating how they can be controlled by materials- and device-design is therefore crucial for breaking existing efficiency limitations. The goal of this project has been to develop techniques which allow the quantum mechanical manipulation of spin states in organic semiconductor devices under device operating conditions. A quantum mechanical (so-called coherent) control of device current, light emission, and other electrical and optical properties allows the most direct way to observe spin-depended processes. The development of these investigative methods was the focus of the first project year (2009-2010). In the second and third year, the work shifted towards the application of these techniques for the investigation of organic light-emitting diode (OLED) structures and mesoscopic organic/inorganic semiconductor heterostructures which could be of technological relevance for light harvesting in third-generation (nano-structure based) solar cell technologies.

FY 2012 HIGHLIGHTS

One important accomplishment of this project during fiscal year 2012 is the demonstration of electrically-detected magnetic resonance (EDMR) at room temperature and, at the same time, extremely low magnetic fields (as low as 1.5 mT). Under these conditions, spin-polarization of charge carriers is virtually non-existent and, therefore, conventional electron spin resonance experiments are impossible. The successful measurement of EDMR at such low magnetic fields is important as these experiments allow the observation of spin-dependent processes under conditions which are close to or within operation conditions of existing device concepts. Furthermore, as this demonstration enables a magnetic field independent determination of the gyromagnetic ratio, it can be used as an ideal natural magnetic field standard. By providing an accurate frequency (which is straightforward in the age of quartz oscillators), OLED devices can be used as highly accurate, calibration free, low-cost thin-film 3D magnetic resonance magnetometers.

Fundamental Studies of Unconventional Sulfide Semiconductors for Cost- Effective and Environmentally Benign Thin Film Photovoltaics

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Funding:	$300,000

PROGRAM SCOPE

This project is focused on the detailed fundamental studies of the structural and electronic defects in the material system $Cu_2ZnSn(S,Se)_4$ (CZTSSe), which is of interest for thin film photovoltaics. In the current three-year project period, our investigation will focus on: (1) measuring and understanding the electrical behavior of grain boundaries in CZTSSe and compositional effects at and near them using bulk and nanoscale electrical and compositional measurements; (2) measuring electronic defects in CZTS, CZTSSe, and CZTSe thin films using electrical spectroscopies and understanding their effects on material properties; (3) modeling point defect equilibrium in CZTSSe guided by *ab initio* calculations and experimental data; (4) spatially-resolving the interdiffusion and reaction of elements and phases during annealing of CZTSSe precursor stacks using element-specific x-ray transmission microscopy and tomography at Stanford Synchrotron Radiation Lightsource (SSRL); and (5) high-resolution Raman studies on CZTS, CZTSSe, and CZTSe as functions of composition to elucidate peak shifts related to point defects and nanoscale phase separation.

FY 2012 HIGHLIGHTS

We highlight three contributions in FY 2012: (1) the completion of a study of CZTS films combinatorial-synthesized at NREL using Raman scattering to correlate the phases present at different growth temperatures with composition, (2) a study of the temperature-dependent through-thickness electrical conductivity of CZTS as a function of composition and annealing time, and (3) the development of a model for predicting point defect equilibrium in CZTS as a function of composition and sample synthesis.

The Raman study showed clearly that for low sample growth temperatures, even for very Zn-rich conditions, the CZTS phase coexists with three polytypes of Cu_2SnS_3 and ZnS. It also showed that the results of bulk and thin film co-evaporative growth are substantially similar (i.e., strain and surface energies are insufficient to cause differences). The conductivity experiments suggested that in polycrystalline films grain boundary, barriers of 100-150 meV dominate the room-temperature behavior while the intragranular disorder- induced hopping dominates at low temperature. The Cu concentration had little effect on the activation energies, while the Zn concentration changed the high temperature activation energy. This was interpreted as signs that Zn influences the doping more strongly.

Thermodynamic, Kinetic, and Electrochemical Studies on Mixed Proton, Oxygen Ion, and Electron (Hole) Conductors

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Funding:	$158,000

PROGRAM SCOPE

The goal of this project is to investigate multi-species transport in predominantly ion-conducting membranes, both theoretically and experimentally. While the primary materials selected are mixed proton, oxygen ion, and electron (hole) conductors, the results of this study are applicable to all electrochemical systems. The selected materials are electrolytes for fuel cells, electrolyzers, and batteries. Transport is examined in the general framework of non-equilibrium thermodynamics. A key feature of our work is the analysis of transport in which thermodynamic forces are expressed as functions of thermodynamic fluxes. This allows the determination of the chemical potentials of electrically neutral species in terms of the fluxes of electrically charged species. The significance is that although chemical potentials cannot be easily measured, fluxes of electrically charged species can be measured as electrical currents. The approach affords the determination of the chemical potentials of hydrogen or oxygen in fuel cell membranes; or of lithium in lithium-ion battery separators, in terms of experimentally measureable parameters, currents, voltages, and transport resistances. Within the framework of linear non-equilibrium thermodynamics (Onsager equations), the analysis shows whether or not chemical potentials of electrically neutral species in the membrane are bounded by values at the electrodes, which is governed by the relative directions of ionic and electronic currents through the membrane. If ionic and electronic currents are parallel, chemical potentials in the membrane can exceed electrode bounds. Should this occur, the membrane and the electrochemical device can degrade. The results explain why fuel cells, electrolyzers, and lithium-ion batteries degrade—and under what conditions. Fundamental reasons for failures of electrochemical devices reside in the basics of non-equilibrium thermodynamics. Experimental verification of the analysis is achieved by the measurement of local thermodynamics in systems that are not in global thermodynamic equilibrium using embedded probes. The long-term impact of this work will lead to the development of degradation-resistant automotive batteries and hydrogen fuel cells—central to the development of the next generation of ‘clean’ automobiles.

FY 2012 HIGHLIGHTS

We have theoretically investigated transport in reversible fuel cells and driven fuel cells. It is shown that Onsager reciprocity relations are applicable in all three modes of transport. Most importantly, the analysis shows that thermodynamic instabilities occur in electrolysis mode and in driven fuel cell mode. In lithium-ion batteries, thermodynamic instabilities occur during charging and during discharge of battery packs due to cell imbalance. In both cases, the introduction of some electronic conductivity in predominantly ionic conducting electrolytes tends to maintain chemical potentials in a stable range and thus minimizes electrochemical degradation—and increases reliability.

Classical and Quantum Stress Effects in Nano Thin Films and in Doping of Semiconductors

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Funding:	$144,000

PROGRAM SCOPE

This project carries out theoretical investigations of strain-induced self-assembly and self-organization of nanostructures in heteroepitaxial growth of thin films and physical phenomena associated with the quantum electronic stress (QES) effect. The main objective is to achieve a better fundamental understanding of stress (strain) effect on physical behaviors of materials, focusing on two specific topics: (1) towards quantitative understanding of heterogeneous nucleation of strained islands on patterned substrate—particularly quantum dot molecules (QDMs)—and (2) quantum manifestations of bulk stress effect in doping of semiconductors and surface stress effect in nanofilms. A multi-scale approach has been employed that combines several state-of-the-art theoretical and computational techniques, ranging from density-functional-theory based first-principles electronic structure calculations to continuum linear elastic theoretical modeling. In the first topic, quantitative analyses will be performed by combining first-principles surface energetic parameters with continuum elastic theory to investigate nucleation, growth, and shape stability of strained islands on patterned substrates, focusing on Si/Ge QDMs. In the second topic, extensive first-principles electronic structure and stress calculations will be carried out to reveal the novel QES effect, which has an electronic origin, rather than the classical stress effect originated from atomic and lattice size difference. Our studies will significantly improve our fundamental understanding of effects of stress/strain on physical behavior of materials, specifically in strain-induced nanoscale assembly and in doping of semiconductors. Our latest discovery of quantum stress effect will likely open up a new subfield in the research of stress effect on physical behavior of materials. Our studies may provide useful guidelines for future experimental efforts in strain engineering of formation of nanostructures and doping of semiconductors. They also have direct technological impact on advancing electronic and optoelectronic materials for energy applications, to fulfill the mission of the Department of Energy.

FY 2012 HIGHLIGHTS

A recent highlight is our rigorous theoretical formulation of QES (σ^{QE}) within density functional theory, in relation to deformation potential of electronic states (Ξ) and variation of electron density (Δn), $\sigma^{QE}=\Xi\Delta n$, as the quantum analog of classical Hooke's law. In the next period, we plan to apply the concept and formulation of QES to simulate and explain structural phase transitions, such as amorphourization, induced by pulse laser irradiation.

Elucidation of Hydrogen Desorption Mechanisms from Complex Metal Hydrides interacting with Carbon Nanostructures

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Funding:	$75,000

PROGRAM SCOPE

The goal of our project is to provide a basic understanding of the interaction of hydrogen with metal atoms supported on carbon nanostructures and examine their physicochemical properties. Our theoretical work is a joint effort with the experimental group of Dr. Ragaiy Zidan at Savannah River National Laboratory. This study is aimed at attempting to predict and control material properties at the electronic, atomic, and molecular level that can form the foundation of new energy technologies. Research is aimed at developing and characterizing a novel class of hydride materials based on metal-carbon nanostructures. The formation of these nano-composites (e.g., Na_XC_{60}) has been of great interest for many researchers in various fields seeking nano materials with novel properties such as hydrogen storage, high ionic mobility, and superconductors. Our work involves hydrogen storage and other properties of a series of M_x-C-H_y nanocomposites.

FY 2012 HIGHLIGHTS

The potential of a variety of nanostructures such as Li functionalized BC_3 nanotubes, Pd atoms adsorbed on activated carbon nanofibers, Ti-doped nanoporous graphene, C_{60} doped $LiBH_4$, Sc- doped pthalocyanine sheet, and functionalized boranes for hydrogen storage was examined. The adsorbed metal atoms are found to store hydrogen in quasi-molecular form driven by the charge polarization mechanism introduced by the PI 20 years ago. Two papers, Highly Porous Borazine-Linked Polymers and Pd Atoms Supported on Nano Carbon Fibers, were published jointly with experimentalists. The work on Li supported C_{60} was in support of the recent experiment in Dr. Zidan's group where the authors showed that Li_6C_{60} can store up to 5 wt% hydrogen reversibly. We provided the theoretical understanding of the structure of Li_6C_{60} and the sites hydrogen atoms bind to. A study of the energetics of the material revealed the manner in which hydrogen is desorbed and the energy necessary for the purpose. Eight papers were published dealing with the interaction of hydrogen with nanomaterials.

Superhalogens and Beyond: Bare and Supported Clusters

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Funding:	$202,000

PROGRAM SCOPE

The goal of the project is to provide a fundamental theoretical 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 exploits the unique size and composition-specific properties of clusters in the atom-by-atom design of a new class of super- and hyperhalogens with unusual composition and properties. They are designed by using simple electron counting rules, such as the octet, 18-electron, and Wade-Mingos, and are used to guide experimentalists in their focused discovery. It deals with four interrelated thematic areas: (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 see if super- and hyperhalogens can also be created without a metal, halogen, or oxygen atom by tailoring their size and composition and if their electron affinities can be pushed to values even higher than that currently known. (2) Next we identify suitable counter ions and explore the ability of their corresponding salts to store hydrogen. (3) Superhalogens with magnetic moments are designed using transition metal atoms as key components. (4) Using electronegative species as building blocks, we explore the potential of multifunctional nanoparticles with Janus anisotropy for clean energy solutions.

FY 2012 HIGHLIGHTS

Working closely with experimentalists, we have been able to identify a new class of magnetic superhalogens with composition $(MnCl_2)_xCl$ (x=1, 2, 3…). Unlike conventional superhalogens that contain a metal atom at the core, the core of these superhalogens is $(MnCl_2)_x$ with each Mn carrying a magnetic moment of 5 Bohr magneton. Similar synergy has also led to the discovery of hyperhalogens containing noble metal atoms (Cu, Ag, Au) at the core and BO_2 superhalogen moieties as ligands. Potential of metal doped carbon fibers, nanoporous carbon, as well as BC_3 nanotubes to store hydrogen was examined and results were complemented with experimental work. Work on functionalized and patterned graphine has revealed unusual electronic, catalytic, and magnetic properties. Our efforts have resulted in 22 publications since the beginning of 2012.

Mesoscale Design of Magnetoelectric Nanocomposites

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Funding:	$217,000

PROGRAM SCOPE

This research program between Virginia Tech (PI D. Viehland and S. Priya) and Rutgers University (A. Khachaturyan) focuses on investigating the mesoscale physics and chemistry of two-phase (magnetostrictive and piezoelectric) magnetoelectric (ME) epitaxial oxide layers. The specific objectives are to (1) develop self-assembling magnetostrictive/piezoelectric nanocomposites having near-periodic nanostructures with giant magnetoelectricity; (2) develop complex and patterned 3-D ME structures where one might be able to demonstrate the effect of orientation and size effects on ME coupling leading to controlled E-field tuning of the magnetization; (3) extend the two-phase self-assembly approach to other multifunctional systems, with the goal of developing new and unique combinatorial properties; (4) develop miniaturized integrated ME layers with self-biasing features; and (5) use 3D Phase Field theory to model nanowire formation, determining the conditions that result in the formation of regularly spaced nanowire structures which maximize their ME coupling.

FY 2012 HIGHLIGHTS

We have made progress in the following areas. (1) Electric field control of magnetic anisotropy in $CoFe_2O_4/Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ heterostructures, and how a domain rotation induced strain can affect the magnetic and magnetoelectric (ME) properties. We have discovered giant magnetoelectricity in an integrated layer for the first time. (2) Growth and characterization of polycrystalline piezoelectric and ferromagnetic substrates with unique properties, and of multiferroic thin films on the polycrystalline substrates. We believe our results in this year provide several novel aspects towards design of the magnetoelectric composite structures. (3) We advanced phase field theory by introducing the transformation strain as a relaxing parameter. This made possible the investigation of giant functionalities in two-phase nanostructured alloys. We then performed 3D computer prototyping of the microstructure formation and evolution under external fields, and established conditions for achieving the enhanced functionalities in some specially chosen two-phase alloys.

Optical Properties of Doped ZnO Nanocrystals and Ceramics

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Funding:	$151,000

PROGRAM SCOPE

Zinc oxide (ZnO) is a potentially important material in electronic devices, including transparent contacts in solar cells, transparent anodes in polymer light-emitting diodes, and active materials in solid-state white lighting. ZnO nanocrystals provide wavelength tunability via quantum confinement and may be useful in dye-sensitized solar cells. Despite the large amount of research performed on semiconductor nanoparticles in general, the fundamental properties of dopants in nanocrystals are only beginning to be understood. *P*-type doping, required for most practical device applications, has been elusive.

The proposed work will use a range of experimental techniques to elucidate the microscopic structure, charge state, and concentrations of defects and dopants in ZnO nanocrystals. The effect of particle size on these properties will be investigated from the nanometer to micron size regimes. To probe energy levels, the band gaps will be tuned by systematically varying quantum confinement, alloy composition, and hydrostatic pressure. By controlling defects and dopants, we aim to achieve *p*-type conductivity in ZnO nanocrystals. Reliable *p*-type doping would be transformative, enabling a range of new applications.

Specific aims of the project include (1) determining the microscopic structure of H complexes in ZnO nanocrystals; (2) investigating the effect of particle size on dopant concentration and charge state; (3) probing H and Cu energy levels as a function of quantum confinement, alloying, and pressure; (4) investigating the effect of Cu doping on the optical properties of ZnO nanocrystals and ceramics; and (5) achieving *p*-type doping of ZnO nanocrystals.

Optical spectroscopy, performed at Washington State University (WSU) and University of Idaho (UI), will be complemented by DOE user facilities at Pacific Northwest National Laboratory (PNNL) and Lawrence Berkeley National Laboratory (LBNL).

FY 2012 HIGHLIGHTS

We performed optical and electrical experiments on nitrogen in ZnO, as well as acceptors in ZnO nanocrystals. These studies provided evidence that nitrogen is a deep acceptor in bulk ZnO and is unsuitable for p-type doping. Nanocrystalline ZnO, on the other hand, appears to contain a 0.46 eV acceptor defect that could point the way toward p-ZnO. In addition to publications, the research was presented in invited talks at the 2012 American Physical Society March Meeting and Materials Research Society Fall Meeting. Students participated in research at WSU, UI, and LBNL's Advanced Light Source.

In Situ NMR Studies of Hydrogen Storage Systems

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Funding:	$190,000

PROGRAM SCOPE

Sodium alanate ($NaAlH_4$) is a model compound for hydrogen storage applications. However, the details of the hydrogen chemistry of this compound upon heat cycling remain unclear. A recent discovery by our group found a previously unidentified mobile metal-bearing species that manifests in the hydrogen chemistry of sodium alanate. Such a mobile species does not appear in the accepted reaction scheme of this compound, and its existence is thought to be important in the reassociation of the sodium and aluminum atoms that phase-segregate upon heating.

The current aim of this project is to use in situ NMR in conjunction with a variety of characterization techniques to study the origins, effects, and consequences of this new species in sodium alanate and related compounds.

FY 2012 HIGHLIGHTS

The mobile Al-bearing species, termed S105, has been extensively studied over the past year. S105 is found to be catalyzed by the presence of hydroxides in the alanate; indeed, in the temperature and pressure regimes we have explored, S105 does not appear in alanate samples not containing hydroxides. Additionally, the proportion of S105 is increased in samples prepared with smaller alanate grain sizes, either by grinding or ball-milling. A variety of techniques including x-ray diffraction, neutron scattering, thermoanalytic techniques, and MAS NMR have been employed in addition to in situ NMR to characterize this chemical species. Furthermore, calculations performed using density functional theory are helping us gain insight into thermodynamically possible crystal structures and compounds that are consistent with the experimental data compiled thus far.

We have also found that hydroxides, specifically NaOH, have a significant effect on the atomic mobility of both Na and H atoms in sodium hydride (NaH). We have published a paper describing this effect during the last year, and we continue to explore the reasons for and implications of this discovery. We will continue to pursue work on these two compounds over the next year, as well as extend our search for analogous atomic mobility enhancements in borohydride compounds and other complex hydrides.

High-Throughput Preparation and Characterization of Vapor-deposited Organic Glasses

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Funding:	$24,000

A summary for this program was not available at press time.

Coupling Electrons, Phonons, and Photons for Nonequilibrium Transport Simulation

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Funding:	$162,695

PROGRAM SCOPE

In order to describe the generally time-dependent and far-from-equilibrium physics of the electronic system that is electrically or optically excited, a full picture of coupling between electrons, lattice, and electromagnetic wave dynamics becomes necessary. This three-pronged interplay, where simulations proceed in parallel at every time-step and drive each other, is what makes theoretical treatment of realistic transport problems far from equilibrium very different from the linear-regime transport and very challenging. This project addresses this knowledge gap.

The objective of this project is to develop a general and efficient multiphysics simulation framework where electron transport, phonon transport, and electrodynamics will be coupled self-consistently and provide insight into the time-dependent and nonlinear transport in optically or electrically excited low-dimensional electron systems. To achieve this objective, electronic transport [simulated by the Wigner Monte Carlo technique] will be self-consistently coupled with the transport of phonons [described by the semiclassical ensemble Monte Carlo technique] and electromagnetic field dynamics [described by the finite-difference time-domain technique and molecular dynamics for subgrid Coulomb interactions].

FY 2012 HIGHLIGHTS

The project started on September 1, 2012. During its first month, we commenced work on Wigner function simulation of a two-barrier tunneling structure and on coupling electronic and thermal Monte Carlo for the simulation of high-field vertical transport in nanostructures.

Complex Hydrides - A New Frontier for Future Energy Applications

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Funding:	$545,000

PROGRAM SCOPE

Every energy-related application of hydrogen (H_2) requires safe and efficient storage. H_2 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 H_2 required for fuel cells. Solid hydrides ensure high volumetric density of the fuel because, in many of them, the volumetric density of H_2 at ambient conditions is nearly twice that of a cryogenic liquid at 20 K, reaching 120 g H_2/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 2012 HIGHLIGHTS

Li-Assisted Dehydrogenation of Ammonia Borane: The mechanism of thermochemical dehydrogenation of the 1:3 mixture of Li_3AlH_6 and NH_3BH_3 (AB) has been studied by solid-state NMR spectroscopy and theoretical calculations. The activation energy for the dehydrogenation is ~110 kJ mol^{-1}, which is lower than for pristine AB (184 kJ mol^{-1}). The major hydrogen release from the mixture occurs at 60°C and 72°C, which compares favorably with pristine AB and related hydrogen storage materials, such as lithium amidoborane ($LiNH_2BH_3$, LiAB). The NMR studies suggest that Li_3AlH_6 improves the dehydrogenation kinetics of AB by forming an intermediate compound $(LiAB)_x(AB)_{1-x}$. A part of AB in the mixture transforms into LiAB to form this intermediate, which accelerates the subsequent formation of branched polyaminoborane species and further release of hydrogen.

Mechanochemical Transformations in $NaNH_2$-MgH_2 System: Mechanochemical transformations occurring during ball milling of sodium amide ($NaNH_2$) with magnesium hydride (MgH_2) have been investigated using XRD and solid-state nuclear magnetic resonance (SSNMR) techniques. For the $2NaNH_2$–$3MgH_2$ system, the mechanochemical reaction proceeds via the formation of MgNH as an intermediate, whereas magnesium nitride (Mg_3N_2), sodium hydride (NaH), and hydrogen (∼5 wt%) form as the final products. The overall solid state reaction for this system is $2NaNH_2 + 3MgH_2 \rightarrow Mg_3N_2 + 2NaH + 4H_2$. However, the mechanochemical transformation of the $2NaNH_2$–MgH_2 system proceeds through the reaction $2NaNH_2 + MgH_2 \rightarrow Mg(NH_2)_2 + 2NaH$, without any hydrogen release. Compared with thermochemical transformations of the same systems, identical final products form via different reaction pathways.

Extraordinary Responsive Magnetic Rare Earth Materials

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Funding: $1,161,000

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 2012 HIGHLIGHTS

Magnetic and structural properties of single crystalline Er_5Ei_4: Magnetization measurements show that even in the true paramagnetic state, there is a weak magnetic field dependence of the structural-only transition when the field is applied along the *a* and *c* axes, but this transition is magnetic field independent along the *b*-axis in fields of 70 kOe or less. The temperature and magnetic field dependent x-ray powder diffraction study of the powdered single crystal confirms the temperature-driven structural orthorhombic-monoclinic transition in the paramagnetic state and also the low temperature magnetic field driven monoclinic-orthorhombic transition in the magnetically ordered state.

Interstitial Impurities: A Tool to Control Magnetic and Structural Transformations: The Gd_5Ge_3 compound prepared using high purity gadolinium undergoes a structural deformation from the hexagonal Mn_5Si_3-type structure into a new orthorhombic crystal structure. When prepared using a commercial grade of gadolinium, Gd_5Ge_3, shows only a minor orthorhombic structural deformation at T_N, which is 19 K lower compared to that made from the high purity Gd. The first principles calculations confirm the antiferromagnetic (AFM) orthorhombic structure as the ground state of Gd_5Ge_3, and show that interstitial impurities affect the strength of the AFM interactions.

Proximity Effects in Conducting Oxide Heterostructures

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Funding:	$1,313,000

PROGRAM SCOPE

This program controls heterointerfacial charge in epitaxial complex oxide thin film heterostructures to beneficially increase ionic conductivity and influence ferroelectric behavior. We create charged interfaces to enhance mobile oxygen vacancy concentrations and suppress oxygen vacancy ordering. Polarization in ferroelectric layers is used to control interfacial charge and oxygen transport in adjacent ionic conductor layers. Conversely, we explore how the electrical boundary conditions imposed by charged interfaces impact polarization behavior in ferroelectric films. The resulting knowledge is furthering basic understanding of charge interactions near interfaces and has great potential to impact energy-related technologies. Our approach employs forefront in-situ synchrotron x-ray scattering and spectroscopy techniques. We determine depth-resolved atomic-level structure and composition in real-time, both during thin film growth and post-growth, in the elevated temperature, controlled oxygen pressure conditions where behavior is most interesting. The program integrates experimental measurements with a theoretical effort that uses first principles calculations to elucidate the factors that control growth behavior and properties.

FY 2012 HIGHLIGHTS

We determined the equilibrium polarization structure of ultrathin $PbTiO_3$ films on $SrRuO_3$ electrodes epitaxially grown on $SrTiO_3$ (001) substrates, as a function of temperature and the external oxygen partial pressure (pO_2) controlling their surface charge compensation [M.J. Highland et al., *Phys. Rev. Lett.*, 107, 187602 (2011)]. We found that the ferroelectric Curie temperature (T_C) varies with pO_2 and has a minimum at the intermediate pO_2, where the polarization below T_C changes sign. The experiments are in qualitative agreement with a model based on Landau theory that takes into account the interaction of the phase transition with the electrochemical equilibria for charged surface species. The paraelectric phase is stabilized at intermediate pO_2 when the concentrations of surface species are insufficient to compensate either polar orientation. This study is currently being extended to examine the interplay between ferroelectricity and ionic conductivity, by growing and characterizing thin film epitaxial heterostructures combining a ferroelectric layer ($PbTiO_3$) and a material that, when doped, exhibits oxygen ionic conductivity (e.g., $LaGaO_3$ or ZrO_2). A new sputter deposition system mounted on a diffractometer was also designed, constructed, and commissioned. Studies of the growth and electrical behavior of $LaGaO_3/SrZrO_3$ heterostructures were initiated. The heterointerfaces in this system allow exploration of the interplay between polar (LaO and GaO_2) and neutral (SrO and ZrO_2) planes, with the possibility of controlling electrical compensation mechanisms to induce or enhance ionic conductivity.

Complementary computational studies began exploring the energetics of interfacial oxygen vacancy formation and migration in the same heterostructures.

Superconducting Materials

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Funding:	$714,000

PROGRAM SCOPE

This program studies the 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 improving the critical temperature T_c, the upper critical field H_{c2}, and the critical current density J_c because they determine limits to energy applications. Because of recent developments and new opportunities, research activities focus on the following.

(1) Systems where superconductivity may be active simultaneously across several different electronic bands like iron chalcogenides. This could provide new strategies for enhancing T_c and H_{c2}, and new superconductors capable of enduring-fields well above 50 T at low temperatures.

(2) Response and control of superconducting transport properties by structural tuning, where the simultaneous increase of $J_c(H)$ and reduction of the J_c anisotropy ratio can be achieved by tuning the defect structures.

Coordinated studies involve synthesis, structural characterization, transport, magnetic property characterization, and expertise in the Condensed Matter Physics and Materials Science Department (CMPMSD). We seek to understand and control the transport properties of superconducting materials by tackling the key science issues, from the macroscopic to the atomic levels. These activities are aligned with the Grand Challenge for the BES Directorate to understand strongly correlated electron behavior in materials and with the Core Research Activities of BES. It brings together a unique synergism between this Superconducting Materials program and other world-class programs at BNL, as well as leading industrial collaborators. Connections to the ARPA-E programs and leading HTS wire manufacturers provide unique technology drivers for this program to respond rapidly and aggressively to new developments, and the access spans vertically from very basic physics and materials questions, through synthesis and structure and property characterization, to finished forms of superconductors that are used in various energy applications.

FY 2012 HIGHLIGHTS

Iron chalcogenide ($FeSe_{0.5}Te_{0.5}$) thin films of record high T_c and J_c were made. Highly effective CeO_2 buffer layer was discovered to be able to promote epitaxial film growth of superconducting $FeSe_{0.5}Te_{0.5}$, reduce the detrimental effect of grain boundaries, and compress the out-of-plan lattice constant of the films that exhibit record high T_c (35% higher than their bulk counterpart) and record high J_c: $2.5x10^6$ A/cm^2 in self-field and $2x10^5$ A/cm^2 in over 30 Tesla external magnetic field at liquid helium temperature. Furthermore, the films made on CeO_2 buffered bi-axially aligned flexible metal substrates

(Ni-W) demonstrate similar high performance to those made on CeO_2 buffered single crystalline substrates (YSZ). The successful CeO_2 buffer concept opens a new research field on the science and technology of iron-based superconductors for energy applications. (*Nature Communications* – in press).

Synthesis and Characterization of Nanomaterial Heterostructures and Assemblies: Investigation of Charge and Energy Flow at Nanostructured Interfaces

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Funding:	$694,000

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 and the foundation of rigorous device development. As highlighted in the DOE reports on Basic Research Needs for Solar Energy Utilization and for Solid-State Lighting, nanostructured materials offer several potential advantages for meeting the energy challenges in these areas by providing for relatively high electron and hole transport efficiencies, excitation multiplication possibilities, high surface-to-volume ratios, and short electron-hole diffusion lengths to junctions. Although it is tempting to combine distinctive nanomaterial components for solar conversion in order to take advantage of such attractive qualities, the fundamental role of nanoscale interfaces and heterojunctions in controlling charge and energy flow is not well understood; and it is expected that junctions and interfaces between low dimensional materials will behave differently as compared with bulk junctions and interfaces. In order to develop an understanding of charge and energy flow at the interfaces of nanostructured materials and nanomaterial assemblies, we will investigate a key model system, namely the interface between a quantum dot and a quantum wire in a heterostructure configuration. We will address the important question of the efficiency of charge separation versus recombination. Furthermore, we will investigate the ability of nanomaterial assemblies to enhance optoelectronic properties of nanoscale components in order to advance their incorporation into functional device configurations. Working with our theoretical collaborators, these studies will help to clarify the role of interfaces and heterojunctions in heterostructured nanomaterial assemblies.

FY 2012 HIGHLIGHTS

Thus far, we have begun to make progress in preparing and eventually providing for a consistent series of samples of identical double-walled carbon nanotube (DWNT)-CdSe and single-walled carbon nanotube (SWNT)-CdSe heterostructures, wherein the ligand-capped CdSe QDs nominally measure ~3.6 and 4.3 nm in diameter, respectively, for both optical and transport measurements. We have also generated control samples, consisting of thiol-capped-CdSe QDs, oleate-capped QDs, raw SWNTs, and DWNTs, as well as their oxidized, ‘purified’ counterparts. It has appeared from the preliminary electron microscopy images of samples analyzed that longer nanotubes may need to be grown, so as to ensure a reasonably clean and purified outer surface and density of tubes for additional characterization and functionalization. From the theoretical perspective, we have been working on source code that will enable us to model non-equilibrium phenomena that will, for instance, analyze what happens when the excitonic spectrum of tubes is perturbed by the presence of quantum dots and vice versa.

Characterization of Functional Nanomachines Program

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Students:	2 Postdoctoral Fellow(s), 3 Graduate(s), 0 Undergraduate(s)
Funding:	$940,000

PROGRAM SCOPE

This project establishes a multi-disciplinary team at LBNL with the goal of understanding and developing mechanical devices at the molecular level. These nanomachines will be engineered at the atomic scale for the purpose of controlling energy and information via mechanical transduction processes. Two paths will be followed toward this goal. First, naturally occurring biomotors will be explored and harnessed to take advantage of the molecular mechanisms provided by Nature. Second, new synthetic molecular machines will be purposefully designed in a molecule-by-molecule fashion. This research will clarify the processes by which nanomachines convert different forms of energy into directed mechanical activity, as well as how these processes are affected by different environmental dissipation mechanisms. The program is aimed at creating new classes of functional nanomachines, such as bottom-up-fabricated synthetic molecular machines that operate on surfaces, top-down-fabricated carbon-based nanomachines that exploit the electromechanical properties of nanotubes and graphene, and hybrid nanomachines composed of integrated synthetic and biological components. These efforts will help to form the basis of a new molecular-mechanical nanotechnology with applications in areas of importance to DOE. Such areas include chemical and photo-sensing, computation, power generation, nanofabrication, and active surface control.

FY 2012 HIGHLIGHTS

Thus far we have developed a new technique for exploring the infrared (IR) vibrational response of surface-bound molecules using the tip of a scanning tunneling microscope as detector (IR-STM). We have additionally succeeded in imaging the photoswitching properties of individual azobenzene molecules adsorbed to clean GaAs crystal surfaces. Suspended graphene nano-oscillators have been fabricated with drumhead diameters down to 30nm, and new techniques have been developed for positioning single nanocrystals at surfaces. RNA polymerase mutants were synthesized for transcription rate studies, and new photoswitching spiropyran derivatives were developed for incorporation into virus packaging biomotors. In the next period, we will work to increase our IR-STM spatial resolution down to the single-molecule level. We will also work to incorporate photoswitching molecules onto electrically gated graphene surfaces, and we will utilize new "straintronics" concepts to enhance our graphene nano-oscillators. We will test hypotheses regarding possible mechanisms of nanocrystal mechanical translocation within nanotubes, and we will use new transmission electron microscopy imaging techniques to explore biomotor locomotion along DNA strands. We will additionally develop new techniques to induce self-assembly of nanomachines at surfaces, as well as explore hybrid nanomachines that integrate both natural and synthetic components.

Electronic Materials Programs

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Students:	0 Postdoctoral Fellow(s), 6 Graduate(s), 0 Undergraduate(s)
Funding:	$1,451,000

PROGRAM SCOPE

The goals of the Electronic Materials Program are to advance and expand the fundamental understanding of the materials science of semiconductors. The research focuses on the relationships between synthesis and processing conditions and the structure, properties, and stability of semiconductor materials systems. Specifically, we focus on three research themes: (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; and (3) control of phase transitions at the nanoscale. Common to these research themes is a synthetic strategy that allows control of 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 2012 HIGHLIGHTS

We have recently reported for the first time the quantum unit of absorptance in 2D semiconductors. By transferring ultrathin membranes of InAs onto optically transparent substrates, detailed absorption studies are performed. Stepwise absorption is observed for the explored thickness range (3-18 nm), arising from the interband transitions between the 2D subbands of InAs. Interestingly, the absorptance magnitude associated with each step is found to be 1.6±0.2%, independent of thickness. The experimental results are consistent with the theoretically predicted absorptance quantum of $A_Q \approx 8\pi\alpha/(3n_r)$ for each set of interband transitions in an ideal 2D semiconductor with asymmetric carrier effective masses, where n_r is the refractive index and α is the fine structure constant (submitted 2012). In addition, we have developed intentionally doped CdO based transparent conductor with record low resistivity of $5x10^{-5}$ ohm cm and transparency window extending from 400 to 1500 nm. The material offers a potential for replacing increasingly expensive silver grids in silicon and high efficiency multijunction solar cell technologies [J. Appl. Phys. 111, 123505 (2012)]. In a separate project, in collaboration with U. Notre Dame, we have resolved a longstanding controversy and demonstrated that the holes mediating the ferromagnetic order in GaAs:Mn are located in the Mn impurity band rather than the valence band. The properties of the holes are described by our band anticrossing model developed for the highly mismatched alloys [Nature Mater. 11, 444, (2012)].

Nanocomposite Proton Conductor

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Funding:	$425,000

PROGRAM SCOPE

This multi-investigator program designs, synthesizes, and evaluates rare earth phosphate materials for proton conducting applications in the temperature region of 300-450 degrees Celsius. The program relies on three major approaches: a theoretical understanding of proton conduction in rare earth phosphates with quantum chemical computation and molecular simulation; the chemical design, synthesis, and conductivity measurement of nano-composite and bulk materials expected to exhibit facile proton conduction; and the structural and dynamic characterization of the nano-composite materials using a range of advanced characterization methods including nanoscale structural and chemical electron microscopy, vibrational and x-ray spectroscopy, and nuclear magnetic resonance. First-principles methods are developed to provide a general basis for computer-aided materials design of ABO4 compounds for proton conductor applications, with A=RE and B=P, V, Nb, and Ta. The associated range of inter-oxygen bond lengths and lattice symmetries are expected to correlate with large variation in proton conductivities. A comparison of theoretical predictions, observed conductivities, and dynamic analyses provides an insight into the fundamental nature of proton conduction at the atomic level.

Nanostructured Materials for Thermoelectric Energy Conversion Program

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Students:	3 Postdoctoral Fellow(s), 5 Graduate(s), 0 Undergraduate(s)
Funding:	$1,090,000

PROGRAM SCOPE

Thermoelectric energy conversion or refrigeration is attractive due to the very high reliability, long cycle life, and lack of moving parts. In spite of these advantages, many thermoelectrics are daunted by low efficiency, high cost, and lack of scalability. In response, this program is scoped to investigate how nanostructuring can improve thermoelectric performance for materials that have the potential to be scalable, low cost, and efficient. The efficiency of such devices is quantified by a dimensionless figure of merit, $ZT = S^2\sigma T/\kappa$, where S is the thermopower or Seebeck coefficient, and σ and κ are the electrical and thermal conductivities of the material. Increasing ZT has historically been extremely difficult due to the coupling between these thermoelectric parameters. Our approach to this problem is to identify paradigms at which these parameters can become decoupled by unique transport phenomenon at the nanoscale and improve the performance. We uniquely focus our attention on new, scalable materials that exhibit unique transport phenomenon rather than on conventional high ZT materials. By understanding fundamental nanoscale energy conversion in these materials, we are able to develop new classes of improved materials that would otherwise go undiscovered.

FY 2012 HIGHLIGHTS

We have successfully demonstrated our deep understanding of transport in organic-inorganic hybrid materials by developing and optimizing the performance of a new, water processable, thermoelectric material. Our work has pioneered a new field of polymeric-based hybrid thermoelectrics, and we are currently in the process of demonstrating how these principles extend to several other polymeric materials. We have also furthered the understanding of transport in silicon nanostructures. We have been able to fully characterize the surface roughness that is responsible for a decrease in thermal conductivity and an enhanced ZT. We have extended that knowledge to silicon ribbons introducing holes which behave in a similar manner to a roughened surface. In the next period, we envision pioneering a never investigated, new phenomenon which we are calling *ionocalorics*. Our preliminary investigation suggests that this area of research has the promise to open another new class of materials for nanoscale thermoelectric energy conversion.

Spin Functionality through Complex Oxide Heteroepitaxy

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Students:	0 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding:	$250,000

PROGRAM SCOPE

The primary goal of this program is to develop novel complex oxide thin films and heterostructures that will lead to an understanding of the nature of magnetism at surfaces and interfaces and emergent spin polarized properties. Our focus in this materials program is on atomically precise complex oxide thin films and heterostructures with magnetic functionality where the surfaces and interfaces play a critical role in the realization of the long-range magnetic order. These materials comprise a new class of oxide materials that may form the basis for the development of more energy-efficient spin-based electronics. Complex oxides exhibit a wide range of magnetic, electronic, and optical properties that can be tuned by parameters such as lattice strain and chemical substitution. The tunability of their structure and properties make them ideally suited for the development of novel thin films and heterostructures with magnetic or spin polarized functionality. We study two novel classes of spin-polarized materials: (1) complex oxide heterostructures in which the interface gives rise to spin polarized properties that are not found in the constituent materials and that are due to modulation doping, carrier mediated exchange, or charge disproportionation; and (2) complex oxide materials, in particular the cobaltate perovskites, in which ferromagnetism is observed in thin film form but not in the corresponding bulk counterpart. In the case of the oxide heterostructures, a sharp interface between two carefully chosen oxide materials as well as atomically accurate delta doping enables us to probe the effects of modulation doping, carrier-mediated exchange, or charge disproportionation that may give rise to magnetic properties at the interface not present in the two oxide materials. In the case of the single-layer thin films, a well-defined sharp interface with the substrate enables us to probe the role of epitaxial strain and non-equilibrium growth techniques on the generation of long-range magnetic order.

FY 2012 HIGHLIGHTS

We have recently demonstrated that metallicity can be generated in thin film form from materials that are Mott insulators in the bulk. More specifically, we have recently found that epitaxial films of $LaVO_3$ and $LaTiO_3$ can exhibit metallicity though their bulk counterparts and are Mott insulators. When $LaTiO_3$ films are compressively strained on $SrTiO_3$ substrates, we observe metallicity that is attributed largely to epitaxial strain-induced electronic structure modifications and secondarily to interface electronic reconstruction at the $LaTiO_3/SrTiO_3$ interface. However, when $LaVO_3$ films are compressively strained on $SrTiO_3$ substrates, the observed metallicity is primarily attributed to interface effects. These results indicate the importance of competing effects of charge transfer at interfaces and lattice-induced electronic structure modifications in this family of materials.

Spin Polarized Functionality through Complex Oxide Heteroepitaxy

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Sr. Investigator(s):	
Students:	0 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding:	$250,000

PROGRAM SCOPE

This program is focused on a strategic materials issue associated with the increasing demand for new electronics from energy, information, and national security technologies: the development of oxide thin films and heterostructures with spintronic functionality. The primary goal of this program is to develop novel complex oxide thin films and heterostructures that will lead to an understanding of the nature of magnetism at surfaces, interfaces, and emergent spin polarized properties. Atomically precise complex oxide thin films and heterostructures with magnetic functionality comprise a new class of oxide materials that may form the basis for the development of a more energy efficient spin-based electronics. Therefore from a fundamental materials perspective as well as a technological perspective, this research is relevant to the DOE BES mission. More specifically, we will (1) design and synthesize complex oxide materials with new magnetic functionality, (2) obtain a fundamental understanding of the nature of magnetism by developing and characterizing novel magnetic ground states in oxide thin films and heterostructures, (3) develop close collaborations with colleagues at LBNL and other DOE labs, (4) act as a resource for thin film materials development, and (5) train the next generation of scientists in thin film materials synthesis.

Sub-wavelength Metamaterial Physics and Applications Program

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Funding:	$650,000

PROGRAM SCOPE

The spectacular on-going development of metamaterials provides an exciting gateway to realize unique and unprecedented optical properties and functionalities not existing in natural materials. These artificially-engineered composites consist of ‘meta-atoms’ or ‘meta-molecules’ that can be tailored in shape and size, where their lattice constant and inter-atomic interaction can be precisely tuned at a deep sub-wavelength scale. In the past decade, impressive progress has been made in the field, covering a wide variety of exotic optical properties. Our program is set up to explore novel physics in optical metamaterials. By careful theoretic design and simulation, we have realized a 3D spherical hyperlens configuration with broadband response and high far-field resolution. And, we have studied the indefinite metamaterial with unique hyperbolic isofrequency contour. We have also investigated the physics of dynamic characters of reconfigurable metamaterials. For the next step, we propose to study novel physical properties and applications originating from new design of optical metamaterials that have never been explored in depth, including advances of metamaterial design with symmetry considerations and inverse electromagnetic algorithm, fabricating reconfigurable metamaterials with new control approaches, and study of new physics in metamaterial hyperlens. We believe that the fundamental discoveries from the proposed research will have profound impact on a wide range of applications in accord with DOE's strategic plans, such as high speed optical communications, imaging, and nanophotonics for energy conversion with high efficiency.

FY 2012 HIGHLIGHTS

We have successfully realized the smallest optical cavity known to date using indefinite materials. Significantly, we found that as cavity size reduces, the radiation quality factor increases dramatically. The unique properties of indefinite cavities will greatly increase the photon density of states and, therefore, enhance light–matter interactions, which may make these cavities valuable for high-performance optical devices. Furthermore, working with terahertz (THz), we have shown a delicate artificial chiral meta-molecule combining with a photoactive silicon medium. Through photoexcitation of the metamolecules with an external beam of infrared light, handedness flipping in the form of circularly polarized THz emission has been successfully observed. Furthermore, the photoexcitation enables chirality flipping and the circular polarization of THz light can be dynamically controlled at high speed. In the next period, we envision these studies will bring new perspectives in the applications of subwavelength light manipulation with metamaterials.

Electrochemically-Driven Phase Transitions in Battery Storage Compounds

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Funding:	$150,000

PROGRAM SCOPE

Compounds of interest for ion storage in advanced batteries frequently exhibit phase transformations, driven by large and variable electrochemical driving forces inherent to practical use. A combined theoretical-experimental study carried out by MIT and Lawrence Livermore National Laboratory will develop a predictive understanding of the interaction between materials variables, such as composition and associated transformation strains; crystallite size and shape, especially at the nanoscale; and electrochemical conditions driving the phase transition, especially the electrical overpotential and its time evolution. Model systems of fundamental and practical interest to be studied include lithium transition metal olivines, $\mathrm{Li}M\mathrm{PO}_4$ (M = Fe, Mn, + additives), and oxide spinels, $LiNi_{0.5}Mn_{1.5}O_4$ and $Li_4Ti_5O_{12}$. Phase-field modeling of phase stability and transformation pathways is combined with in-situ experiments in which electrochemical titration is conducted simultaneously with characterization by synchrotron x-ray diffraction, neutron scattering, and transmission electron microscopy, using DOE facilities. The ability to control phase transformation pathways is expected to lead to new materials design concepts that improve battery performance in categories such as the utilization of active materials at high charge/discharge rates, voltage and capacity hysteresis, and cycling-induced mechanical fatigue affecting life.

FY 2012 HIGHLIGHTS

During the period between September 1st and 30th in FY 2012, phase-field modeling of phase transitions in $LiFePO_4$ that incorporates crystallographic anisotropy effects was initiated. The model was extended to non-spherical and non-cuboidal particle shape to facilitate direct comparison with experiments. The modified phase-field simulation code was implemented on parallel computers, and preliminary numerical testing was completed.

Electronic Processes in Solid State Organic Electronic Materials

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Students:	2 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$441,000

PROGRAM SCOPE

Organic electronic materials are of great intrinsic scientific interest because strong competing interactions produce a rich spectrum of tunable ground and excited states. This makes them an ideal vehicle for the study of flexible strongly correlated systems. The materials are also technologically important for a broad class of applications because of the tunability of their electronic properties, their facile thin film and heterostructure fabrication, and the possibility of creating nanoscale structures and devices through molecular assembly techniques. Because of the very large material and device structure phase space, there is a critical need for basic scientific research on the fundamental physical properties of organic electronic materials. The goal of this project is to provide an understanding of the fundamental physical processes that are important in determining the electrical and optical properties of organic electronic materials. We employ a closely coupled measurement/theory approach aimed at understanding fundamental physical processes in representative model systems and materials, including both conjugated polymers and small molecules. The experimental effort will focus on optical and electrical characterization of model interfaces formed using solution or vacuum deposition techniques. The theory component will connect with these experiments through a hierarchy of microscopic and macroscopic models, including large scale molecular dynamics calculations of the structure at the interface and quantum mechanical determination of the electronic structure associated with a subset of such configurations.

FY 2012 HIGHLIGHTS

(1) Geometric distortions and polarization in conjugated polymers has been examined for a number of electronic excitations in poly-p-phenylene vinylene. These include the lowest singlet (S1) and triplet (T1) excitons, as well as the positive and negative polarons. We also studied the effect of octyl side chains commonly found in the polymers used in actual devices.

(2) Electrical conductivity in organic polymers can be separated into intra-oligomer mobility and inter-oligomer hopping events. In our past work, we identified sites in the amorphous polymer that were

associated with electron and hole trap sites. Those trap sites have strong binding energy for the charge carrier inhibiting the hopping process. In FY 2012, we studied the conductivity along a single oligomer.

(3) Interfaces between different organic materials can play a key role in determining organic semiconductor device characteristics. We developed a physics-based one-dimensional model with the goal of exploring critical processes at organic/organic interfaces. Specifically, we envision a simple bilayer structure consisting of an electron transport layer, a hole transport layer, and the interface between them.

Early Career: Light-Stimulated Epitaxy of Novel Semiconductors and Heterostructures

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

PROGRAM SCOPE

The realization of new semiconductor alloys and heterostructures is critical to materials research efforts, but kinetic limitations often impede the low temperature growth of highly desirable systems. Radically new approaches designed to tailor specific growth processes are needed to overcome these longstanding challenges. The use of light as an additional free parameter to control adatom dynamics has enormous untapped potential and presents a major opportunity in this respect. The principle objective of this research is to use light as an additional free parameter to control adatom dynamics. Specific goals of the project are to (1) transform our basic understanding of growth mechanisms, (2) selectively stimulate and manipulate surface processes that lead to atomistic growth control, and (3) methodically advance the boundaries of semiconductor synthesis and investigation. Experimental measurements will rely on a combination of in-situ and ex-situ analytical tools, such as reflective high energy electron diffraction and light scattering, to explore light-assisted molecular beam epitaxy of III-V semiconductor alloys at low temperatures and II-VI/III-V heterointerfaces. By establishing pathways that surmount current material synthesis constraints, this work will impact the development of advanced approaches to access new growth regimes, facilitate the exploration of novel materials systems, and drive breakthroughs in photovoltaics and solid-state lighting technologies.

FY 2012 HIGHLIGHTS

The state-of-the-art III-V MBE system that will be used for this work was delivered at the end of FY 2012. Additional work involved the design, purchase, and development of infrastructure for a II-VI MBE system, excimer laser beam delivery system, and light scattering measurement system that will be integrated with the III-V MBE.

Electronic and Optical Properties of Novel Semiconductors for Energy Applications

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Funding: $499,000

PROGRAM SCOPE

Advanced energy technologies require high-performance materials, which, in photovoltaics, translates to new semiconductors 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 constraining present photovoltaic and solid-state lighting technologies. It specifically addresses the current unavailability of efficient high bandgap (2.1 eV) and low bandgap (1 eV) absorbers for photovoltaics, and efficient amber emitters for SSL, via technologies based on GaAs substrates. The key to transcending the present limitations is the understanding and control of fundamental electronic and optical processes in semiconductor alloys, which is another goal of this project. Towards this end, the project will focus on understanding the phenomena of spontaneous ordering in high bandgap lattice-mismatched AlxIn1-xP, 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 bipolar Plasmon gasses photogenerated in semiconductors, so as to achieve an understanding of collective phenomena that could enable semiconductors with novel, useful properties. Through collaborative efforts, this project utilizes state-of-the art resources in growth, spectroscopy, and theory, from three national laboratories and two universities, to address the above mentioned issues. By exploiting the use of BES Nanoscience Centers, powerful new tools for the growth and characterization of semiconductors in BES supported DOE Laboratory research are brought to bear.

FY 2012 HIGHLIGHTS

(1) The percolation of impurity states into an electronic band was probed through time-resolved and high magnetic field studies to be a disorder-order Anderson transition. We used high magnetic fields (57 T at the NHFML Los Alamos) to expose and study N supercluster states resonant in the conduction band, by quenching the overlap between N cluster states, thus revealing the reverse order-disorder Anderson transition [*Phys. Rev. B (Rapid Comm.)*, 86, 041201 (2012)].

(2) After over three decades of uncertainty about the exact crossover composition x_c for $Ga_xIn_{1-x}P$ alloys, we were able to precisely determined the value of x_c by simultaneously obtaining a spectroscopic signature of the direct and indirect valleys in a region very close to the crossover composition [*J. Appl. Phys.*, 110, 113701 (December 2011)]. This is invaluable for $Ga_xIn_{1-x}P$ applications in multijunction photovoltaics and solid-state lighting.

(3) We showed that the mechanism underlying an unusual asymmetric lineshape broadening observed in Raman spectra on the dilute nitride alloy $GaAs_{1-x}N_x$ was a Fano interaction between the LO phonon and an electronic continuum [*Phys. Rev. B* 86, 045209 (2012)].

Solar Energy Research Institute for India and the United States (SERIIUS)

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Funding:	$625,000

PROGRAM SCOPE

This 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 is carrying 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 to benefit the U.S.

SERIIUS creates 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 additionally supported by cost sharing from its members. The Consortium comprises 31 partners from India and the U.S.; further information on these organizations and SERIIUS activities is available on its website: www.SERIIUS.org.

FY 2012 HIGHLIGHTS

In April 2012, SERIIUS was notified that it was selected in the solar category of the competitive JCERDC Funding Opportunity Announcement. The start-up activities and accomplishments to date include organization of its partners and establishing SERIIUS management and R&D roles and responsibilities; completion of its research planning involving all its research staff through teleconferences and on-site meetings in the U.S. and India to ensure adequate investments in the three research thrusts; and development of its consensus "Ten-Point Work Plan" for guiding the management and research projects through the task level (including major milestones and deliverables).

Atomistic and Mesoscopic Study of Metallic Glasses

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Students:	2 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$1,005,000

PROGRAM SCOPE

The goals of this project are to gain a fundamental understanding of the science of metallic liquids and glasses and provide guides to the experimental development of new bulk metallic glasses (BMG) with superior properties. 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. In this program, we will advance a fundamental understanding of structural and dynamic properties in metallic liquids and glasses through a combination of tightly-coupled simulation, theory, and experiment. We use a novel approach based upon the concept of topological fluctuations expressed in terms of the dynamics of atomic-level stresses. The computational effort includes molecular dynamics simulations and the first-principles calculation of atomic level stresses. Experimental studies include neutron scattering using the superior power of the Spallation Neutron Source, synchrotron x-ray scattering, and nanoscale mechanical testing. Our goal is to develop a general atomistic understanding of deformation, dynamics, and the glass transition in metallic glasses.

FY 2012 HIGHLIGHTS

Recently we achieved a major advance through the discovery of the elementary excitations in the liquid which determine viscosity at high temperatures. In solids, the elementary excitations of lattice dynamics are phonons. However, in liquids, phonons are strongly damped and have a very short lifetime. We found that the local configurational excitations (LCEs), in which an atom loses or gains one nearest neighbor, are the elementary excitations in the liquid. Using molecular dynamics simulations with classical as well as quantum mechanical methods, we have shown that the time-scale of LCEs, τ_{LC}, is equal to the Maxwell relaxation time, τ_M, for a number of liquid metal alloys at high temperatures. The Maxwell relaxation time (= viscosity/shear modulus) is a macroscopic time-scale of relaxation, whereas the lifetime of LCE is a microscopic time-scale. Thus the atomic-level excitations, LCEs, directly explain the macroscopic behavior of a liquid.

The equality, $\tau_{LC} = \tau_M$, breaks down below the crossover temperature, T_A, below which viscosity rises quickly as temperature is lowered. We found that T_A is the temperature above which phonons are localized, because the phonon mean-free path, $c_T\tau_{LC}$, where c_T is the transverse sound velocity, becomes shorter than the nearest neighbor distance. Thus LCEs cannot communicate with each other through phonon exchange. Below T_A, they interact through phonon exchange and result in a rapid increase in viscosity which culminates in the glass transition. We also found that LCEs are the atomistic mechanism of flow at low temperatures when a glass is turned into a liquid because of high applied stresses. These discoveries mark a major advance in the physics of liquids.

Early Career: Spatially Resolved Ionic Diffusion and Electrochemical Reactions in Solids

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Funding: $500,000

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 2012 HIGHLIGHTS

Within FY 12, Electrochemical Strain Microscopy (ESM) was performed on a variety of battery electrode materials to test the application of this technique for material with different Li-ion storage mechanism. Here, the focus was on the correlation of ESM and the crystallographic orientation to investigate anisotropic ionic transport. The use of temperature-dependent ESM led to spatial resolved mapping of activation energies for ionic transport on the level of individual grains and grain boundaries in layered electrode materials. This information is not accessible with any other technique with the demonstrated spatial resolution and will lead to a better understanding of ionic transport in battery electrodes. In order to implement ESM in liquid environment for in-situ ESM during battery operation, basic electromechanical effects were studied in liquid electrolytes with varying ionic strength. Here, ferroelectrics were used as a model system to establish the boundary conditions for liquid ESM.

Exceeding the Planck Free-Space Energy Transfer Limit through Photonic Density of States Control and Near-Field Coupling

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Funding: $600,000

PROGRAM SCOPE

The objective of the project is to develop a fundamental understanding of, and strategies for, the harvesting of ubiquitous thermal energy in the spectral range where photovoltaic and far-field thermo-photovoltaic approaches are not effective. There are two components to our approach. The first is maximizing the near-field spectral energy density through the utilization of photonic surface states of nanostructures or planar materials. This requires a fundamental understanding of the impact of nano-structuring and material properties on the dispersion and loss of surface photonic states. The second component is developing materials and structures that will enable the extraction of the enhanced near-field energy at rates that exceed the Planck free-space limit.

FY 2012 HIGHLIGHTS

Since the last report, we have continued our studies of indium tin oxide (ITO) as an infrared plasmonic material to enhance and control surface electromagnetic spectral energy. While investigating the surface plasmon mode of ITO, we observed an absorption feature that has not received much attention in the plasmonic community but is better known to optical phonon spectroscopists as the Berreman effect. This absorption feature appears only for p-polarization at an oblique angle, and is associated with the spectral region where the real part of the dielectric function is near zero. While this is a known behavior, the physical understanding of this has never been clearly presented in the literature. We have prepared a manuscript, which will be submitted soon, that presents a much more complete picture of this rather subtle optical phenomenon. In addition, we have investigated the use of metallo-dielectric hyperbolic metamaterials to tune the surface plasmon frequency in the infrared spectral range. Using these subwavelength structures, we experimentally and theoretically demonstrated the tuning of the surface plasmon wavelength from that of pure Au at 0.5 um to about 1.8 um for one of our metamaterial samples. We found that a mean-field theory approach accurately describes the anisotropic dielectric tensor of this material even for a thickness of merely 2.5 periods. The result of this work has been submitted to *Nano Letters* and is currently under review.

On the theoretical front, our collaborator Shanhui Fan has published a work (partially funded by this BES program) in *Applied Physics Letters* showing the feasibility of obtaining near field negative differential thermal conductance between two identical silicon carbide objects. A second theoretical paper is a joint publication with the Fan group that describes a new formalism for the calculation of thermal emission using a combination of temporal coupled mode theory and fluctuation-dissipation theory. This approach enables a clear physical picture of the processes involved and greatly reduces computation time. This manuscript is in the final phase of revision.

Field-Structured Composites

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Funding:	$459,000

PROGRAM SCOPE

The goal of this program is to discover useful methods of manipulating particle suspensions with time-dependent, multi-axial magnetic or electric fields, and to develop a scientific understanding of these phenomena and the impact they can have on technology, including sensing, actuation, microfluidic mixing, and heat and mass transfer. This program on manipulation of materials with multi-axial fields focuses on the development of field-structured composite materials, by using multi-axial fields to create unique particle assemblies that give composites both optimized physical properties and tailorable anisotropy. Physical properties of interest include the magnetic permeability, electric permittivity, and electrical and thermal conductivity. Technological impact is focused on the magnetostrictive actuation of these composites, their use as chemical and strain sensors and thermal interface materials. A significant component of this work involves relating the composite properties to structure with a combination of theory and simulations of structural evolution, and a strong current interest in exploiting anisometric particles such as platelets and nanorods to obtain new effects and new interaction symmetries.

The functional fluid flow thrust focuses on developing methods of using multi-axial magnetic fields to initiate vigorous fluid mixing on the microscale, and to stimulate the formation of advection lattices and rotational flow in fluid suspensions. The advection lattices are a relatively new and surprising discovery that appears to be unique to suspensions of magnetic platelets, and much of our current work is concentrated on exploring the formation of the unique flow patterns and free standing fluid structures we have discovered, and quantifying the attendant heat and mass transfer. These flow patterns have symmetries that are distinct from those produced by natural convection, and offer the possibility of cooling in microgravity environments and transferring reactants and nutrients to a chemical or biological process without extracting heat.

FY 2012 HIGHLIGHTS

We have (1) completed an experimental, theoretical, and modeling study on the thermal conductivity of field-structured composites containing multilayered magnetic platelets that have precisely controlled dimensions; (2) developed a theory of thermal transport in 2-d arrays of elliptic cylinders; (3) discovered a method for creating a fluid vortex lattice in platelet suspensions subjected to spatially uniform ac/ac/dc triaxial fields; (4) discovered that such triaxial fields can also be used to create vigorous rotational flow in platelet suspensions; and (5) completed an experimental study of heat transfer using these rotational flows. The composites work has implications for electrically-insulating thermal interface materials, the suspension dynamics work has implications for noncontact heat transfer and the science of emergent systems, and the conductivity of elliptic cylinder arrays pertains to the development of thermoelectric materials.

Nanometer-Scale Surface and Interface Phenomena

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Funding:	$2,531,000

PROGRAM SCOPE

The goal of this program is to gain a quantitative, atomic-level understanding of principles that control the mechanical, chemical and thermal stability of surfaces and interfaces. Our four major tasks are 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. In all four tasks we focus on materials that both reveal fundamental mechanisms of interest and are relevant to energy technologies. We also develop new theoretical and experimental methods, including Q-force AFM for atomic resolution imaging of insulator surfaces, spectroscopic LEEM-PEEM for correlating spatially resolved electronic structure with surface structure and morphology, and electrochemical scanning probe microscopy to probe surface reactions in electrochemical environments. The project is funded jointly by the Physical Behavior of Materails and Electron and Scanning Probe Microscopies programs.

FY 2012 HIGHLIGHTS

(1) Developed procedures to transfer a graphene sheet grown on a copper surface to one grown a silicon carbide surface to produce a two-layer structure (a bilayer) with varying degrees of rotation between the sheets. (2) Identified van Hove singularities in the electronic structure of twisted bilayer graphene (TBG) in synchrotron ARPES studies. (3) Discovered that TBG on silicon oxide has an unexpected effect on the absorption of visible light. (4) Upgraded our commercial Omicron variable temperature STM with a Q-plus sensor for AFM studies of ice films on insulators. (5) Added energy filtering capabilities and new photon sources to LEEM capabilities for spatially resolved electronic structure measurements. (6) Investigated the order/disorder phase transition on the (100) surface of magnetite. (7) Used electrochemical AFM to show that interfacial layer formation depends on local microstructure during cycling of $LiMn_2O_4$ battery cathodes. (8) Discovered the importance of lithiation rate in determining the resulting structure in Li-Si nanowires using in-situ TEM. (9) Combined scanning x-ray microscopy and TEM to show that intercalation of Li in $LiFePO_4$ proceeds through a particle-by-particle pathway. (10) Discovered initial oxide breakdown structure preceding pit initiation in Al. (11) Developed a finite element model, validated by experimental results, showing that local alkalinity cannot be responsible for pit initiation in Al-Cu alloys.

Elucidation of Hydride Interaction Mechanisms with Carbon Nanostructures and the Formation of Novel Nanocomposites

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Funding:	$430,000

PROGRAM SCOPE

The goal of this program is to support the Office of Basic Energy Sciences mission through the development of a basic understanding of the formation and the physicochemical properties of carbon nanostructures, formed by the interaction of carbon nanomaterials with hydrides and/or hydrogen gas. The purpose of our investigation is to develop control over a material's properties at the electronic, molecular, and atomic level, which will serve as the foundation of new energy technologies and can support other aspects of DOE missions. With this foundation, we will be able to design, synthesize, and characterize new materials for various energy storage applications. More specifically, our research activities will be aimed at developing and characterizing a novel class of hydride materials based on metal-carbon nanostructures. We have previously shown carbon nanomaterials to possess remarkable catalytic effects on hydrogen sorption in complex hydrides. Among several nanostructures investigated, buckminsterfullerene (C_{60}) has been shown to be an excellent catalyst for hydrogen desorption when added to $NaAlH_4$, $LiAlH_4$ and $LiBH_4$. In the $NaAlH_4/C_{60}$ mixture, it was found that the addition of C_{60} lowered the dehydriding temperature and rendered $NaAlH_4$ reversible with hydrogen capacity of 4.3 wt %. A fullerene–$LiBH_4$ composite demonstrated the catalytic ability of C_{60} in two ways by (1) lowering the temperature of hydrogen desorption and (2) regenerating $LiBH_4$ at a relatively low temperature of 350°C. A reversible hydrogen capacity of 4.0 wt % was observed over multiple cycles.

FY 2012 HIGHLIGHTS

We have published two articles supported by this research in *Nano Letters* and *Journal of Physical Chemistry C* which are published by the American Chemical Society. We have demonstrated that a lithium-doped fullerene (C_{60}) can reversibly store 5 wt% at relatively mild conditions. This material was characterized by a series of analytical techniques (XRD, NMR, Raman, FTIR, TGA-RGA, and anelastic spectroscopy) through collaborations with the University of Tennessee, Cal Tech, and Sapienza University of Rome. We are also collaborating with the Institute for Energy Technology (Norway) on neutron diffraction experiments in support of this project. We are currently expanding our research beyond hydrogen storage applications and exploring the possibility of utilizing these and similar materials in other energy storage and conversion devices.

Synthesis and Processing Science

Institutions Receiving Grants

Doping Copper Oxides in Electrolyte Solution: Doping Incorporation, Atomic Structures, and Electrical Properties

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Funding: $203,683

PROGRAM SCOPE

This project pursues a fundamental study of n-type and p-type doping in cuprous oxide (Cu_2O), with the goal of establishing the scientific foundation for solution-based doping techniques for a range of solar energy conversion devices such as next-generation photovoltaic cells and photoelectrochemical cells. Cu_2O provides many advantages over current solar energy conversion devices, including low energy input, low cost, abundant source materials, and non-toxicity—all required for terawatt-scale deployment of these devices. It can be synthesized by solution processes, thus ensuring low-cost device fabrication. Cu_2O is naturally p-type, and PIs' accomplishments demonstrate that naturally n-type Cu_2O can be realized at low pH during electrochemical deposition, and n-type doping in Cu_2O by Cl can be realized during electrochemical deposition. This project attempts to answer several fundamental questions about solution-based doping. The project involves both experimental and theoretical studies to answer the following questions: *Which dopants behave n-type and which behave p-type in Cu2O? What solution-based chemistries incorporate the identified dopants into Cu2O? How do the electrical properties (resistivity, carrier concentration, mobility, conduction type) change with doping?*

FY 2012 HIGHLIGHTS

Formulation of the theory for impurity segregation in electrochemical processes: This provides the theoretical foundation for impurity control in electrochemical processes for doping and purification. The theory points out a clear pathway to low-cost, energy-efficient, solar-grade silicon from metallurgical-grade silicon by electrorefining. A provisional U.S. patent application was filed in April 2012, and a paper entitled "Impurity Segregation in Electrochemical Processes and Its Application to Electrorefining of Ultrapure Silicon" will appear in *Electrochimica Acta*.

Identification of an iron oxysulfide, γ-Fe2O3–xSx, with a direct bandgap of 1.45eV: Despite all the advantages of Cu_2O for solar energy conversion, its bandgap of 2.1 eV is too large for photovoltaic cells. We have conducted a first principles study to find a new semiconductor that possesses all the advantages of Cu_2O but with a direct bandgap of ~1.4 eV. In all the materials we have examined, only γ-Fe2O3–xSx showed a direct bandgap of ~1.4 eV. We are working on demonstrating this new semiconductor experimentally.

Plasmonic Nanostructures Integrated with Semiconductor Light Emitting Materials for Enhanced Efficiency and Functionality

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Funding:	$155,000

PROGRAM SCOPE

The goal of this project is to develop novel metallic nanostructures designed to enhance the efficiency and functionality of semiconductor light emitting materials. Of particular interest are periodic arrays of silver nanoparticles (NPs) fabricated by electron-beam lithography, which can support strong plasmonic excitations (i.e., collective oscillations of the electron gas in a metal) at geometrically tunable wavelengths. The specific materials platform used throughout the project is the family of nitride semiconductors InGaN, whose energy bandgap can be varied across the entire visible spectrum by controlling the alloy composition. Consequently, these materials are technologically important for a wide range of optoelectronic device applications, including solid-state lighting. A major focus of the project is on the use of plasmonic excitations in suitably designed NP arrays to increase the spontaneous emission rate of nearby InGaN quantum wells (QWs), by taking advantage of the highly confined electromagnetic fields and large densities of optical modes associated with these excitations. The overall QW light-emission efficiency can correspondingly be enhanced provided that the NPs are also designed to efficiently scatter the excited plasmonic resonances into radiation. A related goal is the use of similar metallic nanostructures to simultaneously control the properties of the radiated optical beams, such as their degree of collimation, direction of propagation, and polarization.

FY 2012 HIGHLIGHTS

A wide range of plasmonic excitations have been investigated for the purpose of controlling radiation processes in nearby QWs, including localized surface plasmon resonances of Ag NPs, lattice surface modes of diffractive NP arrays, and hybrid resonances of coupled thin-film/NP-array systems. Large enhancements in the QW light output intensity (up to a factor of nearly 5) have been obtained by carefully addressing the critical balance between plasmonic absorption and radiative scattering in metallic NPs. Furthermore, similar plasmonic interactions have been employed to demonstrate substantial collimation of the QW output light and beaming along geometrically tunable directions. The same measurement results also provide direct information about basic properties of the plasmonic excitations involved, including their local field enhancements, resonance wavelengths and/or dispersion curves, and scattering efficiency.

A Unified Understanding of Residual Stress in Thin Films: Kinetic Models, Experiments and Simulations

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Funding: $217,000

PROGRAM SCOPE

Residual stress is a longstanding problem in thin film growth that affects film performance and limits their applicability. The goal of this program is to develop a quantitative understanding of why this stress develops and how it depends on the growth conditions and material properties. The work is centered around the development of a model focused on the stress that develops at the grain boundary as new layers are added to the growing film. The resulting stress is a balance between the generation of tensile stress (due to attraction between the atoms in adjacent islands) and compressive stress (due to insertion of atoms into the grain boundary driven by the supersaturation of adatoms on the surface). The balance between them changes as the microstructure evolves from isolated islands, through coalescence and into a uniform film, leading to a sequence of stress states observed during growth. The model further predicts that the stress in the steady-state depends on the dimensionless parameter D/LR where D is the diffusivity, R is the growth rate, and L is the grain size. Experiments using wafer curvature will measure stress in real-time to refine and test the predictions of this model for different materials systems and deposition methods. Measurements during the early stages of growth will quantify the correlation between the stress and the evolving microstructure (grain size, nucleation rate). In collaboration with Sean Hearne at Sandia National Laboratories, experiments on patterned films will control the point of coalescence for comparison with the model predictions. Collaborations with Hanchen Huang at U. Connecticut will use Kinetic Monte Carlo (KMC) simulations of polycrystalline growth to produce realistic microstructures for input into the model. Other effects such as surface roughness evolution will be measured simultaneously with the stress to determine their effect on the stress. The experimental studies will ultimately be extended to the study of binary alloy systems to look at the effects of the kinetics of the two components as well as the thermodynamic interactions between the two species.

FY 2012 HIGHLIGHTS

This program (only begun in September 2012) supported the completion of an invited critical review article in *Thin Solid Films* (“A kinetic analysis of residual stress evolution in polycrystalline thin films“) that describes the kinetic model in the context of the literature on residual stress. We have been told this article will be featured on the cover of the journal. It also supported calculations that were done for this paper, e.g., using the model to fit data on stress in Ag films and showing the effect of the evolving grain size on stress in the steady-state regime. We have extended the model to the coalescence of islands with spherical shape (instead of the previous cylindrical shape) to understand the difference this has on the evolving stress. Preliminary calculations compare the model with data taken on patterned thin films by Sean Hearne’s group that show the effect of island shape, spacing, and the growth rate. Further work is being done to finalize these calculations for publication.

Mechanisms of Sputter Ripple Formation: Coupling Among Energetic Ions, Surface Kinetics, Stress and Composition

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

PROGRAM SCOPE

Self-organized pattern formation holds the promise of creating nanoscale surface structures over large areas based on fundamental physical processes rather than an applied template. Low energy ion bombardment has been shown to induce the spontaneous formation of a wide variety of interesting morphological features (e.g., sputter ripples and/or quantum dots), but the underlying mechanisms are not well understood. This program is focused on understanding the processes controlling sputter ripple formation, providing unique insight into the kinetics controlling the evolution of surfaces and nanostructures, and including conditions occurring in high flux environments such as nuclear reactors. This is done by using systematic, quantitative experiments to measure ripple formation under a variety of processing conditions. This has enabled us to develop a kinetic phase diagram of the pattern formation behavior, to show how different regimes of pattern formation depend on the temperature and flux. Continuum models based on an instability mechanism demonstrate that the measured evolution can be explained within this simple paradigm. Kinetic Monte Carlo simulations confirm that the atomistic mechanisms included in the continuum model lead to the type of patterning behavior predicted. Recent work has focused on understanding the effect of other mechanisms besides sputtering (such as ion-induced stress) on modifying the ripple formation kinetics. Measurements and calculations of the stress induced by low energy ion bombardment and its effect on ripple formation are enabling us to establish the connection between them.

FY 2012 HIGHLIGHTS

We have quantified the stress that develops during low energy ion bombardment of Si surfaces and developed a model to explain the measured flux dependence. Unlike previous experiments at higher energies, we find that there is a pronounced flux dependence to the stress (high energy experiments showed a dependence on ion dose but not flux). This indicates that there is an effect of ion-induced defects on the stress relaxation process. We developed a model that includes the effect of ion-enhanced viscous flow due to defects in the layer. The viscous relaxation depends on the concentration of “flow” defects created by the ion beam. However, the model also includes the process of defect annihilation to explain why the relaxation does not persist after the ion beam is turned off. This model is able to successfully explain the measured flux dependence and provide parameters for the kinetics of defect annihilation. Most importantly, it is able to estimate the amount of fluidity per defect, which has not been determined previously. Simultaneous measurements of the stress and pattern formation indicate that the induced stress does not modify the ripple wavelength or growth rate, in contradiction with the continuum model.

Thermochemistry of Oxides with Electrochemical and Energy Applications

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Funding:	$250,000

PROGRAM SCOPE

The major objectives of this project are to (1) 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, and (2) 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 (AxRE1-xMyM’1-yO3 (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 (Bi2O3-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.

The materials under study find important applications in solid oxide fuel cells, gas separation membranes, catalysts, batteries, as well as nuclear energy and aerospace applications. Thus they are directly relevant to the development of more efficient energy sources and energy utilization.

FY 2012 HIGHLIGHTS

Triplite and tavorite iron-manganese fluorosulfate polymorphs were thoroughly characterized prior to acid solution calorimetry. This calorimetric study shows that, although both are similar in energy, the disordered triplite has greater stability above room temperature because of the entropy associated with its disordered structure. Samaria doped, neodymia doped, and samaria/neodymia co-doped ceria were synthesized and characterized. We have synthesized defect fluorite-phase dysprosia-stabilized bismuth oxides. Thermochemical measurements were made by high temperature oxide melt drop solution calorimetry.

Enthalpies of formation of synthesized samples from their binary oxides were determined by high temperature oxide melt solution calorimetry. The endothermic enthalpy of defect formation of interstitial oxide ions and cation vacancies was calculated. Also, it is found that $La_8Sr_2(SiO_4)_6O_2$, having neither vacancies nor interstitial oxide ions, is the most stable compound in these two series.

Atomic Layer Deposition (ALD) of Metal and Metal Oxide Films: A Surface Science Study

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Funding:	$200,000

PROGRAM SCOPE

This project focuses on developing a molecular-level understanding of the thermal reactions that organometallic compounds used for atomic layer deposition (ALD) follow on surfaces. ALD is poised to become one of the dominant technologies for the growth of nanometer-sized conformal films in many industrial applications. In microelectronics in particular, the growth of diffusion, adhesion, and protection barriers and of metal interconnects is central to the buildup of diodes, transistors, and other elements within integrated circuits. All of these processes require the deposition of isotropic films on complex topographies under mild conditions and with monolayer control. ALD is particularly suited to satisfy all of those conditions, but many questions concerning the underlying surface chemistry need to be answered before it can find widespread use.

Our mechanistic studies of the ALD-related reactions is being pursued with the aid of a number of surface-sensitive techniques, including X-ray photoelectron, Auger electron, low-energy ion scattering, temperature programmed desorption, and infrared spectroscopies. Our initial focus has been on the study of processes for the deposition of metal interconnects and of metal nitride and metal oxide films, both central components in the microelectronics industry. Specific questions are being addressed in terms of the kinetics and mechanisms of the reactions involved, and also in connection with the composition and morphology of the resulting films. This knowledge will be directed to the design of ALD processes that operate under the mildest conditions possible and deposit stoichiometric and pure films with good density, low resistance, and smooth surfaces.

FY 2012 HIGHLIGHTS

We have made progress on several fronts. We have continued to characterize the surface chemistry of copper precursors for ALD, specifically of $Cu(acac)_2$ on Ni(110) and Cu(110) surfaces. Chemical transformations were identified in several steps covering a temperature range from 150 K to at least 630 K: (1) desorption of Hacac and 3-oxobutanal (CH_3COCH_2CHO) at 150 K and 180 K on Ni(110) and at 160 K and 185 K on Cu(110), respectively; (2) partial loss of the acetylacetonate (acac) ligands and a likely change in adsorption geometry, with the possible production of HCu(acac), which desorbs at 200 K and 235 K from the nickel and copper surfaces, respectively; (3) molecular $Cu(acac)_2$ desorption on both surfaces at approximately 300 K, with reduction to metallic copper; and (4) further decomposition of the organic ligands. Additional work was performed to study the deposition of Mn films with $Mn_2(CO)_{10}$ and $MeCpMn(CO)_3$.

Non-Equilibrium Effects in the Processing of Materials Using Plasmas

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Funding:	$100,000

PROGRAM SCOPE

Non-thermal plasmas have emerged as an efficient, controllable technique for generating small semiconductor nanoparticles with good control over their size, structure and surface chemical termination. These nanoparticles have many interesting properties that could open the door to significant improvements in technologies including light-emitting diodes, photovoltaic panels, batteries, and thermoelectric devices for waste heat recovery.

This project will improve our understanding of the interaction between the nanoparticles and the partially ionized gas in which they are nucleated and grown—a crucial process that is not well characterized today. For instance, there is not a clear understanding of why silicon particles with different structures or surface chemical composition can be obtained by tuning the plasma parameters. The plasma research community has already gained a deep knowledge of the chemical processes that lead to the nucleation of nanopowders, but has yet to focus on the influence of plasma parameters on the nanoparticle materials properties. This project will address this knowledge gap through well-controlled experiments. A continuous flow non-thermal plasma reactor will be used to nucleate and grow silicon nanoparticles starting from an argon-silane gas mixture. In-situ Fourier transform infrared spectroscopy (FTIR) will be applied for the first time to a plasma reactor that is deliberately optimized to generate nanoparticles with controlled properties. The nanoparticle surface will be monitored as it is directly exposed to the plasma-generated radicals. The data obtained by this technique will be correlated with measurements of plasma parameters such as ion and atomic hydrogen density. In-situ FTIR will also be used to measure the temperature of the nanoparticles as they are confined in the plasma reactor. This will be achieved by using metal-organic molecules with a well-characterized dependence of the infrared (IR) absorption spectrum over substrate temperature. These molecules will be deposited onto small nanoparticles, which then will be sent through a non-thermal plasma reactor. Their IR absorption will be measured as the particles are in direct contact with the partially ionized gas. Simple numerical models will be developed to predict the effects of the exposure to plasma-produced radicals on the particle temperature and surface configuration, and to compare them with the experimental data.

By the end of this project, a detailed description of the interaction between non-thermal plasma and nanoparticles will be reached. This is of crucial importance, since the compatibility of nanomaterials with a variety of applications depends strongly on their structural and surface properties, which in turn strongly depend on the techniques that are used to synthesize them. This knowledge has the potential to open the door to U.S. leadership in a new technique for manufacturing electronic and energy devices.

Synthesis and Engineering of Sub-Monolayer Type-II Quantum Dots to Enhance Material Properties of Wide Bandgap Semiconductors

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Funding: $200,000

PROGRAM SCOPE

Semiconductor heterostructures whose conduction and valence band alignments are ‘staggered’ are typically referred to as type-II heterostructures. In this program we investigate type-II quantum structures, such as ZnTe quantum dots embedded in a ZnSe matrix, in an effort to understand and exploit their tunable optical and electrical properties, by taking advantage of the type-II band alignment and quantum confinement effects. Previously, a high net acceptor concentration of 6×1018 cm-3 was achieved for ZnSe by the migration enhanced molecular beam epitaxy (ME-MBE) technique, incorporating N within the ZnTe nanoclusters embedded in the ZnSe, while keeping relatively low overall content of Te. Unfortunately, this material exhibits rather low free hole concentrations. It was concluded that the conductivity of the layers remained low most likely due to the localization of the holes in the valence band wells resulting from the large valence band discontinuity (~0.7 V) between ZnTe and ZnSe. To modify the band structure and reduce the localization of the holes, samples were grown with Mg added to the ZnTe QDs. Initial characterization showed that the Mg was contained primarily within the QDs, which exhibited typical type-II QD behavior, and that, for the first time, we were able to measure free hole concentrations using Hall effect, supporting our hypothesis that the band offset of the new ZnMgTe QDs, and consequently the hole confinement, had been reduced. During this second year funding period, we performed further in-depth structural and optical studies of the ZnMgTe QD structures to better understand their characteristics. We have also used magneto-PL measurements to demonstrate the formation of QDs and to obtain an accurate determination of the QD size. Currently, we have begun to grow and investigate a new type-II QD material system consisting of ZnTe QDs embedded in a ZnCdSe matrix. This material is expected to exhibit desirable new properties, such as long electron lifetimes and a broad absorption spectrum, of potential applications in high performance photovoltaics.

FY 2012 HIGHLIGHTS

During the past funding cycle, our work has centered around two main efforts. First, we have carried out a detailed analysis of the evolution of the QD formation as a function of Te content. We have observed that as the Te content of the material increases, the size of the QDs does not change significantly, while the density increases monotonically until they coalesce into a continuous layer. Secondly, we have grown a new material consisting of ZnTe sub-monolayer type-II QDs embedded in a ZnCdSe matrix, all lattice matched to InP substrates, and begun to characterize this material. The goal is to further develop this material as a potential candidate for the fabrication of intermediate band solar cells.

Asymmetric Hybrid Nanoparticles

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Funding:	$154,000

PROGRAM SCOPE

This project is concerned with the synthesis, characterization, and application of plasmonic nanoparticles and their structures. Plasmonic nanoparticles interact strongly with light and exhibit unique optical properties arising from the excitation of the collective oscillations of the conduction electrons. One of the main emphases in the project is on asymmetric hybrid nanoparticles. These nanoparticles are composed of a silver core capable of supporting plasmon resonances and dielectric shells or caps on the particle's surface. Whereas the shells encapsulate completely the cores, the dielectric caps cover only selected areas of the particle surface. Such asymmetric hybrid nanoparticles exhibit new properties that arise from the interactions between the core and shells and caps, thereby rendering the development of these structures fundamentally and practically important. In addition, plasmonic particles, when in close proximity to each other, exhibit plasmon coupling leading to much stronger cooperative interaction with light and novel optical properties. We target the design of structures for efficient light harvesting applications and for novel optical devices.

FY 2012 HIGHLIGHTS

We have previously discovered that asymmetric plasmonic particles have the ability to scatter light with the polarization orthogonal to that of the incident light. This depolarized light scattering will find many important applications, for example, optical labeling. The main advantage of such optical labels stems from the ability to perform optical imaging and detection on a zero background level. We have completed the comprehensive study of the depolarized light scattering from individual plasmonic asymmetric nanoparticles as well as their dimers, trimers, and tetramers.

Investigating the Metastability of Clathrate Hydrates for Energy Storage

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Funding:	$170,000

PROGRAM SCOPE

Clathrate hydrates or 'gas hydrates' are a class of inclusion compounds that form when water and suitably sized guest molecules come into contact at favorable temperature and pressure conditions. The network of hydrogen-bonded polyhedral water cages of the clathrate hydrate are stabilized primarily by guest-host interactions. The nature of these interactions, size of guest species, and the thermodynamic environment can lead to the formation of different characteristic cages or clathrate structures. With the ability to concentrate gases by approximately a factor of 160 their volume at ambient conditions, clathrate hydrates offer a potential solution for many energy related issues including storage, transportation, and recovery.

Although thermodynamically stable clathrate hydrate structures are well known, the phenomenon known as metastability of clathrate hydrates is poorly understood. This project aims to probe the key questions surrounding the metastability of hydrates relating to synthesis, structure, and composition. The questions on metastability are crucial in all energy applications of clathrate hydrates including energy storage, energy transportation, and energy recovery. Specifically, this project addresses:

(1) self-preservation metastability – hydrates preserved outside equilibrium conditions
(2) structure/phase metastability – coexistence/transitions of metastable phases
(3) metastable cage composition/occupancy – variable cage occupancy and dynamics

These synthesis-structure-stability relations of clathrate hydrates are severely under-explored yet hold the key to successful application and control of clathrate hydrates in all energy applications.

FY 2012 HIGHLIGHTS

Our work has been highlighted by two main accomplishments focusing primarily on understanding structural and cage composition metastability (items 2 and 3 above). Specifically, we have developed a new synthesis method involving incorporation of preformed clathrate hydrate seed crystals, leading to rapid conversion of ice to clathrate hydrates of molecular hydrogen at near liquid nitrogen (LN_2) temperatures (Grim et al., J. Chem. Phys., 2012). Additionally, by extending this new synthesis technique to include pre-formed structure I (sI) hydrates, we discovered H_2 occupancy in both the small and large cage environments of structure I (sI) clathrates, as evidenced by powder x-ray diffraction and Raman spectroscopic measurements (Grim et al., J. Phys. Chem. C, 2012). Prior to this study, H_2 was only observed in structure II hydrate, which demonstrates that large cage occupancy of H_2 and potentially other energy rich gases may be possible for a variety of structures and cages by simply manipulating the synthesis procedure to include pre-formed hydrates.

Directed Assembly of Rod-Coil Block Copolymers by Combined External Fields

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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 π-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 calculations with high accuracy and newly proposed fast off-lattice Monte Carlo 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 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 diblock copolymer 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 2012 HIGHLIGHTS

We have successfully applied the fast off-lattice Monte Carlo simulations to study the order-disorder transition (ODT) of symmetric coil-coil diblock copolymers. Combined with the mean-field (random-phase approximation) analysis for the same model system, our simulations unambiguously quantify the effects of fluctuations/correlations on ODT, which is a classic yet unsolved problem in polymer science. Furthermore, we have developed a computationally efficient soft-core spherocylinder model for the orientational interaction between rod blocks that accounts for their degree of overlapping, and have validated this model by examining its isotropic-nematic transition using both fast off-lattice Monte Carlo simulations and virial expansion. In the next period, we plan to study the self-assembly of rod-coil diblock copolymers based on this soft-core spherocylinder model using both self-consistent field calculations and fast off-lattice Monte Carlo simulations.

Characteristic Length Scales of Growing Nanorods

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Funding:	$170,000

PROGRAM SCOPE

This project focuses on the identification of characteristic length scales of growing nanorods, the formulation of theories governing these length scales, and the realization of science-based nanorod growth. The emphasis is on scientific principles of nanorod growth, in contrast to exotic morphologies of nanorods. With this emphasis in mind, the prototype material of this research is face-centered-cubic Cu.

The research relies on a synergy of theories, simulations, and experiments. The theoretical formulations aim to reveal interdependence of multiple characteristic length scales and their dependences on growth conditions. Atomistic simulations will serve to verify or disprove existing theories and guide the development of necessary new theories. While the combination of theoretical formulations and atomistic simulations can lead to discovery of new characteristic length scales and can predict the transition between growth modes, accompanying experiments serve to validate the discoveries and predictions and often motivate further modeling studies.

FY 2012 HIGHLIGHTS

We have identified two characteristic length scales: the separation of nanorod nuclei and the smallest diameter of nanorods, and their interdependence. The separation of nanorod nuclei has become available in closed form, for the first time, with verification using lattice kinetic Monte Carlo simulations. The smallest diameter of nanorods has become available in closed form, also for the first time. This closed form is accurate under idealized shadowing conditions, and its scaling relationship remains valid under non-idealized shadowing conditions. Augmenting these two closed form theories is the atomistic simulation results. Combining the theories and simulation results, we have pushed the lower limit of smallest metallic nanorods. Specifically, (1) our theories have enabled the explanation of an anomalous transition of growth modes and (2) our experiments, which are directed by the theories, have achieved the smallest metallic nanorods via physical vapor deposition that have not been achieved before—specifically, Cu nanorods of 20-25 nm and Au nanorods of 10-15 nm.

In addition to the planned research on length scales of growing nanorods, the atomistic simulations have driven us to an “accidental” discovery—a new method of interatomic potentials. Recognizing the limitation—in addition to the wide use—of the embedded atom method (EAM), we have proposed and developed a response EAM (R-EAM) that have two major advantages over EAM. One, the R-EAM potentials do not impose the three unphysical constraints on elastic constants of crystals, as EAM potentials do. Two, R-EAM potentials provide a qualitatively better description of surface outward/inward relaxations than EAM potentials do. These two advantages make the R-EAM particularly useful for simulations of crystalline nanomaterials including nanorods; beyond this project, it is particularly critical and advantageous for low symmetry metallic solids and alloys.

Self-Assembly of Non-Spherical Colloids: New Reduced Symmetry Crystals and Mesophases for Templating Functional Materials at Fine Scales

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Funding: $200,000

A summary for this program was not available at press time.

Using Interfaces to Create Strongly-Coupled Magnetic Ferroelectrics via Atomic-Scale Heteroepitaxy

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Funding: $340,000

PROGRAM SCOPE

In this program, we are developing the scientific ideas necessary to apply a materials design paradigm to the creation of multiferroics with unprecedented coupling between ferroelectric and magnetic order parameters, i.e., strongly-coupled magnetic-ferroelectrics. This project has two research objectives. The first 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, but we recently predicted a class of materials that we call hybrid improper ferroelectrics where octahedral rotations are exploited to enable such switching. 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. Our second objective is to create magnetic ferroelectrics where the magnetism can be turned on by applying an electric field. Such an effect has also never been demonstrated, but we predicted it to occur in appropriately strained $EuTiO_3$. Our subsequent observation of a strain-induced ferromagnetic ferroelectric state in strained $EuTiO_3$ confirms the microscopic coupling model and calculations underlying this prediction. The simultaneously ferromagnetic and ferroelectric state that we induced in $EuTiO_3$ with strain created the world's strongest ferromagnetic ferroelectric, in agreement with our first-principles prediction. This verification strongly motivates our desire to turn on the strong ferromagnetism in appropriately strained $EuTiO_3$ by the application of a modest electric field. By creating new interface phases and atomically thin layers, we are achieving, through rational design, materials systems that provide the structural and magnetic properties—which are often mutually incompatible in bulk systems—needed to realize such a strongly coupled magnetic-ferroelectric.

FY 2012 HIGHLIGHTS

Using first principles calculations, we showed that the strong coupling between the rotations of oxygen coordination octahedra in complex oxides (a type of lattice distortion that is ubiquitous in complex electronic materials) and magnetic properties represents an opportunity to understand and create new multiferroics. We established general design rules and identified new classes of materials (i.e., known Ruddlesden-Popper phases as well as artificial superlattices) that should exhibit such behavior. Our work showed, for the first time, how octahedral rotations simultaneously induce and thereby naturally couple ferroelectricity, magnetoelectricity, and ferromagnetism—a breakthrough in the field of multiferroics. The new octahedral-rotation-based mechanism enables an applied electric field to globally and deterministically switch the magnetization by 180° in a single-phase multiferroic material.

Following our materials-by-design approach, we have grown epitaxial thin films of the materials identified by reactive molecular-beam epitaxy and are characterizing their structure and properties. One of the experimental issues that we have run up against is the difficulty in switching the materials we have made to date through the application of an electric field. This difficulty has motivated our theory effort to identify materials within this new class of multiferroics having lower activation barriers to switching.

Improved Electrochemical Performance of Strained Lattice Electrolytes via Modulated Composition

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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. Here, we use sputter deposit nanostructured multilayers of oxygen ion conductors. The multilayers are composed of materials where all layers can support ionic transport. A few series of well-controlled compositional modulations enable the determination of the relative importance of strain and defect formation and association energy in redistributing the mobile defects. High resolution TEM, EELS, and SIMS are used to physically characterize the specimen. Impedance spectroscopy determines the effects of the layer spacing and the magnitude of compositional modulation on both ionic conductivity and surface exchange. Oxygen ion conductors, with application to SOFCs, are used in this study; however, the concepts and methods discovered are applicable to other ionic conduction systems. The research impacts our understanding of the effect of materials nanostructure upon the ionic conduction and influences the development of methods to engineer improved conduction.

FY 2012 HIGHLIGHTS

This project published on a demonstrated expertise in fabricating ceramic thin films with precisely controlled composition, which can vary as a function of lateral position or thickness. In particular, reactive sputtering using elemental targets of Ce, Zr, Y, and Gd has been used to fabricate films with arbitrary composition. By calibrating the deposition rates from each target separately and then correcting for subtle changes in these deposition rates while co-sputtering, films with arbitrary dopant and host atom composition $Ce_{1-x-y}Zr_xD_yO_{2-\delta}$ (D=Y or Gd) were created. Structure was controlled by the deposition rate, substrate type, and substrate temperature, to create films that were heteroepitaxial single crystalline, polycrystalline with either high texture or random orientation, or amorphous. Specifically, yttria-stabilized zirconia (YSZ) films were epitaxial with (100) orientation when deposited on (100) MgO substrates and strongly (111) textured when deposited on (0001) Al_2O_3. Ceria films (including those with Gd dopant) were similarly textured on Al_2O_3 substrates but had random orientation on MgO. Epitaxy could be obtained in the ceria films, however, by first depositing a thin YSZ buffer layer film on MgO. With this unique deposition method, very high purity fluorite films, including multilayers, with thicknesses from monolayers to 100’s of nm with adjustable and precisely controlled composition can be created. A range of single-layer and multilayer films have now been fabricated and electrochemically characterized. A notable increase in the low temperature conductivity of YSZ films has been found as the film thickness decreases below about 25 nm. Gd-doped ceria films exhibited no discernible change in behavior as a function of film thickness. Multilayer films have thus far demonstrated mixed conductivity, with electron conduction dominating over the oxygen ion conduction. The use of isotope exchange experimentation with thin films was additionally explored. To that end, calculations and demonstrations were published on the ability of isotope exchange to measure relevant diffusivity and surface exchange coefficients on mixed conducting thin films.

Discovery and Crystal Growth of New Oxide Phases from Metal Fluxes

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Funding:	$200,000

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, and 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 general low melting point of the 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, 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. With the alkaline earth metal fluxes having simultaneous solubility for oxides, halides, hydrides, and chalcogenides, new phases are expected to form under unusual conditions.

FY 2012 HIGHLIGHTS

Single crystals of a series of $BaLn_2O_4$ phases crystallizing in the CaV_2O_4-type structure were grown from a barium flux. In this structure, the lanthanide ions have a triangular arrangement with potentially frustrated magnetic interactions. The magnetic properties of these systems are under investigation.

A flux comprised of a eutectic magnesium-barium composition showed good simultaneous solubility of oxygen as well as tellurium, leading to the formation of a new phase, Ba_2TeO. The structure of Ba_2TeO is related to LuNiBC and can be regarded as a combination of rock salt type and PbO-type building blocks. With the tellurium p-orbitals predominantly forming the valence band, and the barium 5d orbitals dominating the conduction band, this new phase shows semiconducting behavior. Optical absorption measurements show a broad absorption band in the visible range, and doping experiments have found that the conductivity of this phase can be adjusted over a wide range. For instance, preliminary work has indicated that up to 8at% bismuth can be substituted for tellurium in the structure.

Nanoscale Morphology Evolution under Ion Irradiation

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PROGRAM SCOPE

The use of ion beams has great promise for morphology control in materials synthesis and processing at sub-lithographic length scales. This research program is a combined experimental and theoretical study of the fundamental physical principles governing nanoscale surface morphology evolution during ion irradiation at energies low enough that the principal phenomena are observed at the surface rather than in the bulk.

This program focuses on two distinct but related aspects of nanoscale surface morphology evolution under ion irradiation. (1) In a process called “sputter patterning,” self-organized one- and two-dimensional arrays of nanoscale surface features (“ripples” and “dots”) sometimes form spontaneously on initially flat surfaces. If the medium-range order exhibited by the spontaneous patterns could be guided predictably by lithographically generated templates, then useful periodic structures as small as 7 nm could be generated in high-throughput settings. (2) The ability of ion beams to controllably close nanopores to molecular dimensions in a process called “ion beam nano sculpting” permits the fabrication of solid-state single-biomolecule detectors and may become the basis for nanoscale morphology control in the mass production of a wide variety of nanoscale devices.

FY 2012 HIGHLIGHTS

Our recent work overturns the long-standing paradigm attributing sputter patterning to the effects of sputter erosion of the surface by the ion beam. We have shown conclusively that the effects of erosion are irrelevant for pattern formation. We have done so through two independent lines of inquiry: experimentally, by investigating the pattern-formation “phase diagram” of pattern and wavelength observed vs. “control parameters” such as ion energy and incidence angle and by studying the evolution of the pattern in real time; and theoretically, by characterizing the “crater function”, or average local surface morphology change, arising in molecular dynamics simulations of individual ion impacts. Our observations have led to definitive conclusions because we have concentrated on the simplest possible case – an amorphous, isotropic, monatomic material that is amenable to atomistic simulation. We have proposed a new paradigm, based on the crater function arising from impact-induced atomic redistribution. With no adjustable parameters, our theory, based on this paradigm, attains an unprecedented level of agreement with experiment. The basic understanding gained from these advances may lead to new materials design criteria for stability under irradiation.

Synthesis of New Diamond-Like B-C Phases under High Pressure and Temperatures

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Funding:	$195,000

PROGRAM SCOPE

The aim of the research in this proposal is to synthesize a new class of diamond-like materials containing only boron and carbon, B-C, and to study their properties. The scope of the research proposed is four-fold: (1) to synthesize pure diamond-like B-C phases with C/B ratio lower than 4 (BC, BC_2, BC_3 etc.) by direct conversion of layered graphitic phases with different B and C concentrations over a wide P-T-range up to 70 GPa and 2500°C using a double-sided laser heated diamond anvil cell; (2) to study the effect of P-T conditions on formation of *dl*-BCx phases and the nanostructure of these phases; (3) to determine the atomic structure, bondings, nano-structure, and composition of the novel high-pressure phase(s) using x-ray diffraction, Raman spectroscopy, EMP, XANES, and FIB/TEM/EELS system, respectively, with an emphasis on the composition of nano-grains in novel *dl*-BC_x phases; (4) to characterize the elastic properties of the novel high-pressure phase(s) using the LU-DAC technique and synchrotron-based x-ray diffraction under hydrostatic conditions (e.g., in an inert gas pressure medium).

FY 2012 HIGHLIGHTS

This year, we synthesized a diamond-like BC_x phase with high boron concentration under high pressure and high temperature (HPHT) conditions, and began a full characterization of the B_2C and BC_8 layered system. The new phase, *c*-B_2C, was obtained by direct transformation from a graphitic phase at a pressure of 31 GPa and temperature 2000 K in a laser-heated DAC. The x-ray diffraction technique and Raman spectroscopy measurements confirm the presence of cubic B_2C (*c*-B_2C) from the sample recovered at ambient conditions.

To understand the mechanism of the transformation of graphitic phases with sp^2 bonds to novel denser phases with sp^3 bonds under HPHT conditions, we conducted Raman scattering measurements in graphite and a graphitic *g*-BC_8 phase under high pressure up to 84 GPa. We demonstrated that there is a phase transition in the graphite and the *g*-BC_8 at 35 GPa (sp^2 to sp^3 rehybridization). Above 35 GPa, the *g*-BC_8 phases transforms into a novel high pressure phase, sp^3 bonded amorphous phase, *a*-BC_8.

Studies of the graphitic BC_x phases with high boron concentration revealed the unusual properties of these phases. Brillouin scattering measurements indicate that the *g*-B_2C phase deposited at ambient pressure and 900 K is super-hard. To understand the reason for the unusual elastic properties of the *g*-B_2C phase, we conducted a transmission electron microscopy (TEM) study of this phase. Results of the TEM study allow us to conclude that the formation of a network of randomly distributed boron atoms and sp^2 bonded carbon atoms results in high elastic moduli of the *g*-B_2C phase.

Laser Fabrication of Active Single-Crystal Architecture in Glass

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Funding:	$175,000

PROGRAM SCOPE

This project explores the promises and challenges of nonequilibrium synthesis and processing with lasers beams, specifically the fabrication of 3D single crystal architecture in an infrared (IR) transparent glass. Its goal is to develop the enabling science for the formation of active, ferroelectric (single) crystal-in-glass architecture (FCGA), leading to a new class of IR metamaterials that combine exceptional electrical, mechanical, and optical functionalities of ferroelectrics (FE) with the robustness, easy formability, and low cost of glass. They would provide multiple novel functionalities for micro/nano-opto-electro-mechanical system (M/NOEMS) transducers, sensors, electrically addressable nonlinear waveguides, optical modulation, etc.

We are investigating laser-induced single crystal growth in GeS_2-SbSI chalcogenide glasses (ChG) as a model system, which is IR-transparent and devitrifies normally to form ferroelectric SbSI crystal. The key issues of laser-induced fabrication include (1) controlled single crystal growth by CW lasers under glass→paraelectric→ferroelectric transformation in a relatively soft ChG; (2) the relationship between growth conditions and crystal/domain orientation; (3) the impact of various photoinduced phenomena (such as photofluidity, photodarkening, photoexpansion, etc.), which are special characteristics of ChG on its crystal growth process; and (4) the elemental redistribution under extreme beam power of fs laser. The mechanism of single crystal growth by laser irradiation is being determined as a function of laser characteristics with supporting structural information from electron microscopy, EXAFS, Raman spectroscopy, and advanced surface analysis techniques in conjunction with sputtering. This structural information forms the basis for theoretical modeling of the FCGA fabrication process. The quality of FCGA depends on its ferroelectric response of confined crystals, as governed by crystal order at micron and nanometer scales. It is being characterized by novel spectroscopic techniques pioneered by the PIs. Thus, this comprehensive project is establishing a scientific basis for exploiting lasers in the optimum fabrication of novel FCGAs for various energy technologies.

FY 2012 HIGHLIGHTS

We have fabricated a series of Sb-S-I bulk glasses including stoichiometric SbSI composition, and established successive stages of their modification induced by irradiation with a focused CW Ar+ laser, including structural modification, crystallization, decomposition and strong photocontraction. The latter two phenomena in chalcogenide glasses complicate the formation of FCGA significantly, compared to oxide systems. Laser irradiation causes significant structural and chemical changes from the simultaneous decomposition of SbSI via evaporation of SbI_3, and its crystallization. An unexpected suppression of decomposition by crystallization introduces new possibilities for the laser fabrication processing. The observed SbI_3 evaporation and volume change make 2D micromachining of chalcogenides glass surface feasible by laser irradiation. Together with laser-induced surface crystallization of SbSI ferroelectrics, both passive (optical waveguides, Bragg gratings, microlenses, and lens arrays) and active (electro-optic modulators and wavelength convertors) infrared micro-optical elements can be fabricated in the same glass substrate.

Utilizing Molecular Self-Assembly to Tailor Electrical Properties of Si Nanomembranes

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Funding:	$150,000

PROGRAM SCOPE

The ability to control the synthesis of materials with nanometer precision has the potential to revolutionize technology. However, the utility of engineered nanomaterials for important applications such as photovoltaics, nanoscale electronic devices, and molecular/biological sensors has in many cases been severely limited by interfacial phenomena that emerge at the nanoscale. It is crucially important to understand and control hetero-interfaces between organic and inorganic materials. However, an atomic- and molecular- level understanding of the interfacial phenomena remains elusive. Meanwhile, achieving large-scale in-plane azimuthal molecular ordering on inorganic substrates is still a significant challenge. The objective of this project is to use silicon nanomembrane, a well controlled two-dimensional single crystalline semiconductor, as a prototype system to explore the mechanistic basis of electronic interactions at hetero-interfaces between organic and inorganic materials and to develop strategies to tailor nanomembrane's transport properties by surface functionalization and self-assembly.

This work will (1) explore the principles of self-assembly and organic growth on Si substrates, in particular how the delicate balance between molecule-molecule and molecule-substrate interactions influence the energy landscape and dynamic processes of growth like diffusion and nucleation, and (2) exploit the precision of molecular assembly on Si nanomembranes and combine the scanning probe microscopy characterization of local interfacial electronic structures with the electrical transport measurements of nanomembranes to elucidate the interfacial phenomena. The fundamental insights provided by this research will offer new potential to the integration of ordered organic thin films in silicon-based electronics and rational design of nanomaterials with controlled properties via regulation of surfaces and interfaces.

FY 2012 HIGHLIGHTS

Thus far, we have realized self-assembly of organic molecules and discovered the anisotropic step-flow growth of metal phthalocyanine (Pc) on the deactivated Si surface. Using scanning probe microscopy and geometric modeling, we demonstrated the quasi-epitaxial nature of this step-flow growth, which effectively reduces the substrate symmetry and allows for the formation of metal Pc thin films with an exclusive in-plane azimuthal registration to the substrate. Furthermore, we have investigated the transition of growth modes with temperature on a variety of metal Pc molecules. These altogether show a universal trend, indicating that the novel anisotropic step-flow growth mode we have discovered can be generalized to other organic systems grown on the deactivated semiconducting substrates.

Brush-Coated Nanoparticle Polymer Thin Films

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Funding:	$228,000

PROGRAM SCOPE

Polymer nanocomposites (PNCs) are a technologically important class of materials; they exhibit diverse functional properties, from optical and electronic, to biomedical and structural based on the chemistry and functionality of the polymer host and the functionality, size, and spatial distribution (dispersion or organizational order) of the nanoparticles. One of the primary challenges in this field is associated with control of the nano and macro-scale structure. Because the properties of PNCs depend on the morphological structure, the development of reliable strategies to "tailor" structure of the PNC is essential. One effective strategy is to tether chains onto the surface of the nanoparticle, thereby enhancing the degree of compatibility. The proposed research is to discover and to develop an understanding of interrelations between the structure and specific properties (mechanical, glass transition, optical, dynamics) of thin film polymer nanocomposites (PNCs) containing brush-coated metallic nanoparticles. Our goal is to discover the basic principles that enable fabrication of functional thin film PNC materials with tailored structures and properties. The first objective of our program is to develop an understanding of how interactions between the free chains and the brush layers on the nanoparticles, and the interfaces, determine the morphological structure of polymers.

FY 2012 HIGHLIGHTS

(1) The optical properties of metallic nanoparticles are particularly interesting due to localized surface plasmon phenomena. The optical responses of the nanoparticles are sensitive to the refractive index of their local environments. Consequently, nanoparticles are used for a range of sensing applications. Prior research for this proposal enabled us to work out molecular design principles that enabled us to control the spatial distribution of metallic nanoparticles of various sizes throughout thin films. In doing so, we are able to "tailor" the optical responses of thin film nanocomposites of polymers containing gold nanoparticles of varying sizes.

(2) Hybrid, soft material/nanoparticle composites, materials are useful for a wide range of applications, from sensors to organic electronics. We examined questions related to the manner in which defects influence the organization of nanoparticles within the material. Specifically, we designed and fabricated gold nanoparticle/block copolymer nanocomposites such that the nanoparticles were almost exclusively located within interfacial defects (dislocations). The dislocations form loops of varying size distributions, well described by a theoretical distribution function. The time-dependent evolution of organization of the nanoparticles was examined, for the first time, and is well described by a general theory developed to understand phase ordering in multi-phase materials.

(3) We developed a new electroheological fluid composed of polystyrene spheres sulfonated polyhedral oligomeric silsesquioxanes (s-POSS) mixed with polydimethyl siloxane (PDMS). This ER fluid flows like a normal fluid at room temperature, but exhibits an increase in viscosity by two orders of magnitude upon application of an electric field.

Phase Transformations and Equilibria in Complex Half-Heusler/Full-Heusler Nanocomposites

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Funding:	$340,000

PROGRAM SCOPE

This project focuses on experimental and theoretical investigations of phase formation, phase transformation, and the phase relationships in pseudo-binary half-Heusler/full-Heusler systems—hereafter referred to as HH(1-x)/FH(x) ($0 \leq x \leq 1$)—at various temperatures. Bulk HH(1-x)/FH(x) nanocomposites contemplated in this project consist of a semiconducting HH matrix containing FH quantum dots coherently integrated at the atomic-scale within the crystal lattice of the HH matrix. We will use selected HH(1-x)/FH(x) compositions to investigate (experimentally) the relationship between the aging temperature—aging time—and the microstructure evolution in non-crystalline monophasic HH(1-x)/FH(x) ingots driven far from equilibrium via quenching from the melt. In addition, theoretical calculations of the free energies of the diffuse interfaces between the FH inclusions coherently embedded within a HH matrix, the bulk free energies, and the Ni (or Co) diffusion coefficients between FH inclusions and HH matrix will enable continuum simulations of precipitation kinetics and precipitate coarsening in the HH(1-x)/FH(x) compositions.

These studies will allow full understanding, predictability and control over the mechanism of formation and evolution of integrated FH nanostructures within a HH matrix; the behavior of the FH inclusions over time at high temperatures; and the development of chemical and physical processes leading to fully reproducible growth of HH(1-x)/FH(x) nanocomposites with predefined microstructures.

The embedded FH nanostructures were found to play a key role in discriminating between high energy and low energy carriers within the bulk HH matrix, leading to drastic decrease in the effective carrier density (n) and large enhancements of the carrier mobility (μ). We will explore the effectiveness of FH quantum dots in tailoring the electronic and thermal transport properties in a bulk HH matrix in order to elucidate the underlying mechanism. The goal is to provide a comprehensive suite of materials selection criteria and processing parameters favorable for the fabrication of semiconducting composites in which the formation of coherent nanometer scale matrix/inclusion interfaces results in a large enhancement in the mobility of intrinsic free charge carriers available within the semiconducting matrix.

Understanding and Controlling Nanoscale Crystal Growth using Mechanical Forces

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Funding:	$149,857

PROGRAM SCOPE

Growth of one-dimensional nanostructures such as carbon nanotubes (CNTs) and silicon nanowires is analogous to bulk crystal growth, where a solid is formed by precipitation due to a thermodynamic driving force at an interface. While it is well-known that mechanical stress affects crystal growth, diffusion, and defect migration, the mechanisms and roles of these phenomena at the nanoscale are not comprehensively understood and have not been studied with respect to growth of nanostructures. We suggest that the atomic organization of nanostructures by precipitation from catalyst nanoparticles can be significantly altered by mechanical stresses acting on the growth interface, and that these effects are uniquely important for nanostructures because of their small size and sensitivity to surface forces and interactions. These effects are of further interest because the properties of nanotubes and nanowires can be significantly altered by small changes in diameter, and by incorporation of small numbers of defects.

This research program explores how mechanical stimulation can be used to control the formation rate, geometry, and perfection of one-dimensional nanostructures and will thereby aim to create understanding of how mechanical stress affects the growth of crystals at the nanoscale. To enable this unique investigation, we will create and use instruments for application of controlled forces to one-dimensional nanostructures during growth; and we will employ comprehensive in situ and ex situ characterization to relate the measured growth kinetics and structural transformations of the nanostructures to the imposed mechanical stimuli.

FY 2012 HIGHLIGHTS

We have focused on four primary tasks. The first is the final design and construction of the nanostructure growth and electromechanical control system, for growing nanostructures with in situ mechanical and electrical stimulation. The second task is the validation of CNT pillar manipulation and sensing with the tower system, which is a major subsystem of the first task. We have demonstrated feedback control of force, position, and velocity of the custom linear actuator, along with non-contact sensing of individual CNT pillars. The third task is the analysis of CNT population growth dynamics. By high-resolution spatial profiling of CNT diameter, alignment, and density within CNT forests, we have developed a comprehensive collective model of CNT activation and deactivation kinetics. We have also extracted CNT-CNT coupling forces based on identification of diameter-dependent population kinetics and analytical models of individual CNT lengthening kinetics. The final task is the design and fabrication of a first-generation MEMS device for applying controlled tension to individual CNTs during growth across a micron-scale gap.

Hydrodynamic Self-Assembly of Topographical Patterns on Soft Materials

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Funding:	$80,000

PROGRAM SCOPE

The surface topography of a material can have a significant impact on its optical, adhesive, and wetting properties. The overall objective of this research is to use theoretical tools to explore fundamentally new ways of creating and controlling surface topography on soft materials. Principles from hydrodynamics and self-assembly play a significant role in this research. Examples of synthesis and processing routes that are being explored include electrohydrodynamic instabilities, dewetting-driven instabilities, and evaporation-driven patterning. Materials of interest include polymer solutions, polymer melts, and colloidal suspensions.

FY 2012 HIGHLIGHTS

The principal accomplishment during the past year is the completion of a study examining the influence of viscoelasticity on AC electrohydrodynamic instabilities. Viscoelastic effects are prominent in polymeric liquids and most easily characterized by a relaxation time, a characteristic time scale it takes for stresses to decay to zero if an applied strain is removed. We have successfully extended our prior work on Newtonian liquids [S. A. Roberts and S. Kumar, J. Fluid Mech. 631, 255 (2009)] to account for viscoelastic effects. This was a considerably more challenging problem because (1) the governing equations are much more complicated and (2) the presence of two time scales (the oscillation frequency and relaxation time) makes the problem extremely stiff. Nevertheless, we were able to overcome these challenges and determine that viscoelasticity tends to increase the growth rate of the instabilities but does not significantly change their wavelength. This is contrary to what we expected and may stem from the fact that our analysis ignores inertial effects, which should become important for sufficiently large oscillation frequencies and growth rates. Our results, which are currently being reviewed for publication, point the way for the next stage in this work, the consideration of inertial effects.

Epitaxial Electrodeposition of Metal Oxide Thin Films and Superlattices for Energy Conversion and Storage

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Funding:	$335,000

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 method in which solids are assembled from molecules and ions in solution, much like in 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 (1) electrodeposition of crystalline Co_3O_4 – a potent oxygen evolution catalyst, (2) electrochemical reduction of epitaxial metal oxides to epitaxial metals and alloys, (3) electrodeposition of nanostructured metal oxides (such as manganese dioxide nanowires) for pseudocapacitors, and (4) electrodeposited plasmonic nanostructures for photovoltaics. The research work strongly emphasizes the basic science behind the electrodeposition of epitaxial and nanostructured metal oxides.

FY 2012 HIGHLIGHTS

Our most significant accomplishment this year was the demonstration that crystalline Co_3O_4 can be electrodeposited directly onto substrates. The crystalline films of Co_3O_4 were deposited by electrochemically oxidizing a tartrate complex of Co(II) in aqueous, alkaline solution. The electrodeposited Co_3O_4 was shown to be a very potent catalyst for the oxygen evolution reaction in alkaline solution. In future work, we plan to electrodeposit the material onto n-type semiconductors that will serve as photoanodes for the photoelectrochemical splitting of water into hydrogen and oxygen. The oxidation of water to oxygen is the kinetic bottleneck in the water-splitting reaction. We also plan to study the catalytic activity of electrodeposited $Co(OH)_2$ and CoO_2 for the oxygen evolution reaction. A high-risk, high-payoff research area we are also exploring is the electrodeposition of germanium from aqueous solution. Germanium has semiconductor properties (such as higher carrier mobilities) that are superior to those of silicon, but it is an expensive semiconductor to produce in bulk. Electrochemistry could provide an inexpensive route to produce thin films of the material.

New Pathways and Metrics for Enhanced, Reversible Hydrogen Storage in Boron-Doped Carbon Nanospaces

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Funding:	$320,000

PROGRAM SCOPE

This project is an integrated synthesis/characterization/computational effort to develop monolithic boron-doped carbon made from polymeric precursors, crisscrossed by networks of nanopores, expected to have superior hydrogen storage capacities not available in other materials. The goal is to develop a fundamental understanding of the mechanisms by which boron, through its electron-deficient electronic structure and long-range effect on distant carbon atoms, combined with appropriate pore geometries, creates deep potential wells which could hold films of molecular hydrogen at densities much higher than undoped carbon. Such films and their thermodynamics at the molecular and macroscopic level are critical for the design of high-performance materials with controlled reversible storage characteristics at low pressure and room temperature. The program supports one of the high-priority research directions of the National Hydrogen Storage Project.

FY 2012 HIGHLIGHTS

We have observed anomalous adsorption of H_2 in synthetic carbons, with significantly higher excess adsorption per surface area at both cryogenic and room temperature (approximately twice that of the best lignocellulose, graphene-like carbon). This is consistent with the predominance of 0.7-nm pores in the solid, which host high binding energies. An alternative explanation for the high H_2 uptake was developed, in which pores expand as function of pressure in the range of 10-100 bar as a result of increased adsorption, and is under experimental investigation with elastic neutron scattering. In inelastic neutron scattering of the hydrogen-loaded sample, experiments over an unusually wide range of energy and momentum transfer were conducted at ORNL, which probe the quantum states of adsorbed H_2 and indicate that the carbon matrix hosts planar domains of unexpected extent. Confirmation of the extended planar domains, consistent with observed 700 m^2/g of surface area, was obtained by aberration-corrected scanning transmission electron microscopy (ORNL). The presence of boron-carbon bonds, including sp^2 bonds essential for enhanced H_2 adsorption, was established on reference materials by microscopic Fourier transform infrared spectroscopy and x-ray photoelectron spectroscopy. An adsorption instrument operating at 7-300 K and 0-200 bar has been constructed for measurement of film thickness, area, and density of adsorbed, saturated H_2 films at supercritical conditions (high-density films, 1-2 monolayers thick). Preliminary investigations suggest that such films may behave like a liquid film with fixed volume and density comparable to that of liquid hydrogen, and will vary considerably with temperature and binding energy of H_2 on boron-doped carbon surfaces.

Atomistic Structure, Strength, and Kinetic Properties of Intergranular Films in Ceramics

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Funding:	$142,000

PROGRAM SCOPE

Two fundamentally important issues in materials involve the effect of nanoconfinement on the structure and properties of the nanoconfined phase and the surprisingly important role of these phases on bulk material properties. Thin (1-2nm) amorphous silicate intergranular films (IGFs) that are present in polycrystalline ceramics provide an excellent example of how nanoconfined glasses can play a dominant role in material properties, where, for instance, a change in the minor additive in the IGF causes significant changes in grain growth and mechanical properties. However, obtaining detailed atomistic information about these IGFs has been experimentally difficult and the goal of our program is to evaluate the structure, strength, and kinetic properties of the IGFs at the atomistic level using molecular dynamics simulations. Initially, we addressed the atomistic structure of these IGFs and the role of the bounding crystals on this structure, with resultant predictions that were subsequently verified using the most advanced electron microscopy techniques. We have shown how the interface between the silicate IGF and crystals of silicon nitride, a high-strength high temperature ceramic, attracts a specific rare-earth additive which then attracts certain anion species towards the interface that modifies the resultant composition in the interior of the IGF that modifies the strength of the material. This kind of concerted action provides the mechanism by which this particular rare-earth additive modifies the mechanical properties of the nitride ceramic. Further studies with other rare-earth additives are being conducted and compared to available HAADF-STEM results for atomistic structural verification followed by strength analysis.

FY 2012 HIGHLIGHTS

We are showing how minor changes in the composition of the nitride surface (specific N sites replaced by O) significantly affect the local interfacial adsorption and structure of certain rare-earth additives from the IGF, but not others. This may play the dominant role in the changes in mechanical properties seen experimentally, and we are testing this behavior using simulations of the tensile strength of differently oriented silicon nitride crystals with the modified surface compositions separated by the IGF. Also, recent TEM studies of grain growth in ceramics as a function of the type of separation between the crystals (thick or thin IGFs, mono- or bi-layer film, etc.) show significantly different growth rates but single activation energy. This raises important questions regarding the role of these separating ‘complexions’ on growth, and we are currently addressing the kinetic growth behavior of dissimilarly oriented crystals separated by the IGF.

In Situ Visualization and Theoretical Modeling of Early Stages of Oxidation of Metals and Alloys

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Funding: $150,000

PROGRAM SCOPE

The goal of this project is to develop an atomic-scale understanding of the oxidation of metals and alloys ranging from the initial stages of oxygen surface chemisorption to the subsequent stages of nucleation and growth of bulk oxide. Three research objectives are set to acquire the ability to manipulate the microscopic processes of oxidation: (1) tune oxygen chemisorption induced surface phase transitions via oxygen gas pressure and temperature; (2) tune the crossover from on-surface oxygen chemisorption to subsurface oxygen incorporation; and (3) tailor the growth morphologies of oxide nanoislands via metal/oxide interfacial strain. These studies will exploit the unique in situ capabilities of scanning tunneling microscopy, transmission electron microscopy, and x-ray photoelectron microscopy to dynamically measure the surface structure and surface chemistry under a wide range of oxidation conditions. Each of the experiments will be 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. Due to the decisive role of the environment in determining the reaction behavior, incorporation of the temperature and pressure effect into the first-principle thermodynamics calculations will not only allow for identifying how the interplay between thermodynamics and kinetics determines the final structure, composition, and oxidation mechanism, but will also provide the baseline for tailoring the structures and composition of materials to steer the reaction toward the desired direction.

FY 2012 HIGHLIGHTS

The structure difference between idealized single crystal surfaces and real surfaces containing a concentration of low coordinated sites is known as the structure gap and has been a major obstacle hindering the understanding of the microscopic processes controlling the oxidation of metals. Using in situ atomic-resolution electron microscopy observations, we observe the oxidation of Cu surfaces composed of flat terraces and step edges. Oxidation occurs via layer-to-island growth of Cu_2O on flat terraces, with Cu adatoms evaporating from steps and diffusing across the terraces. This process can be regarded as deposition of a solid oxide from a mixed phase of Cu and O thermally diffusing across the surface, which is rather different from the long-held oxidation mechanism of the solid-solid transformation. This result is significant because it demonstrates that the presence of surface steps can promote the development of a flat metal-oxide interface by kinetically suppressing the solid-solid transformation of oxide formation, thereby allowing for manipulating the oxidation behavior of metals by controlling the surface morphology.

Synthesis and Properties of Nanostructured Exotic Superconductors

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PROGRAM SCOPE

The goal of this project is to develop methods to synthesize a new class of superconducting nanowires and nanoribbons which are stable in atmosphere, enabling the exploration of superconducting properties and potential applications of individual nanostructures.

We have successfully synthesized robust nanowires and nanoribbons of $NbSe_2$ and NbN. Four-probe resistive measurements on these nanostructures revealed intriguing superconducting properties. The synthesis approach we developed consists of two steps: (1) synthesize non-superconducting nanowires and nanoribbons of a compound ($NbSe_3$), which promotes anisotropic growth due to its unique crystalline structure, and (2) convert these into desired superconducting nanostructures ($NbSe_2$ and NbN), which are normally difficult to synthesize, by adjusting the composition of the non-superconducting nanostructures while maintaining their shapes.

By utilizing whisker technologies for nanofabrication by replacing the catalyst microparticles used in whisker growth with the same kind of nanoparticles which could be available commercially or synthesized in our own laboratories, we succeeded in growing nanowires and nanoribbons of high-temperature (high-Tc) superconductors $Bi_2Sr_2CaCu_2O_{8+x}$ and $YBa_2Cu_3O_{7-x}$. These systems provided unique platforms to pursue vortex dynamics in confined geometries and nanoscale superconductivities. We observed new phenomena such as re-entrance superconductivity in pristine samples and driving-force dependent vortex phase diagrams in those containing arrays of nanoscale holes introduced through focused-ion-beam (FIB) milling.

FY 2012 HIGHLIGHTS

We carried out both experiments and computer simulations to investigate the dissipation in superconducting niobium strips with a chain of nanoscale holes. We found large magnetoresistance oscillations and discovered a new dissipation mechanism due to current-excited moving vortices [PRL 109, 057004 (2012)]. We developed a new fabrication method to achieve networks of superconducting nanowires with ultra-small (< 10 nm) transverse dimensions by depositing MoGe onto nanoporous alumina substrates, enabling the observation of phase slippage driven dissipation in a large temperature range and the Little-Parks effect at magnetic fields up to 2 Tesla [PRB 85, 174503 (2012)]. We also carried out magneto-transport measurements and computer simulations to investigate the saturation number and caging effect in a superconducting film containing a honeycomb array of nanoscale holes [PRB 85, 012505 (2012)].

Four-Dimensional Analysis of the Evolution of Complex Dendritic Microstructures During Coarsening

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

PROGRAM SCOPE

Dendrites are tree-like structures that frequently form during solidification of castings. Dendrites possess secondary and, sometimes, even tertiary side branches. While the tip radius and tip velocity of the dendrite are set by the growth conditions, the side branches behind the tip undergo a coarsening process under nearly isothermal conditions. The resulting two-phase mixtures are morphologically complex. These dendritic two-phase mixtures are one example from a large class of morphologically complicated structures found in nature that undergo coarsening. Included in this class are the bicontinuous two-phase mixtures produced following phase separation. Understanding the coarsening process in these systems requires theory, simulation, and experiments that capture their three-dimensional morphology.

At the core of the proposed investigation is a four-dimensional characterization and analysis approach, which follows the morphological evolution process in three dimensions and in time (an additional dimension). A combined theoretical and experimental program is proposed to examine the nature of the coarsening process in these highly complex, dendritic microstructures. The experiments will examine the time-dependent evolution of the dendritic mixtures in three dimensions in situ through x-ray microtomography. The results of these experiments will be used both to provide insights into the coarsening process and to guide the development of theory. Simulations of coarsening in bicontinuous mixtures will be used to develop a theory of coarsening in these systems that will elucidate the importance of the complicated morphology found in dendritic systems on the coarsening process. Through these experiments and theory, we aim to develop a comprehensive description of coarsening in these complex and technologically important two-phase mixtures.

FY 2012 HIGHLIGHTS

We performed time-dependent x-ray tomography of two-phase solid-liquid mixtures. We returned with 14 TB of data to analyze. A 3D reconstruction of the interfacial morphology was used as a cover image on the *Journal of Metals*. Using this data, we have examined the correlation between interfacial velocity and mean curvature. We find that despite the presence of long-range diffusion, the velocity of a point on the interface is, on average, directly related to the mean curvature of the interface. Such a strong relationship would only be expected to hold during interface kinetics controlled interfacial motion, such as grain growth.

We have developed a data smoothing process that allows for accurate determination of the time derivatives of the mean and Gaussian curvatures. This approach was used to examine the evolution of curvature under both interface controlled coarsening (Allen-Cahn dynamics) and bulk diffusion controlled coarsening (Cahn-Hilliard dynamics). Interestingly, we also find that for bulk diffusion controlled coarsening, the velocity of a point on the interface is linearly proportional to the mean curvature.

Conduction Mechanisms and Structure of Ionomeric Single-Ion Conductors

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Funding:	$445,000

PROGRAM SCOPE

Our team of five faculty design and synthesize low glass transition temperature single-ion conducting ionomers that are either polyanions that transport small cations Li^+, Na^+, Cs^+ or polycations that transport small anions F^-, OH^-, Br^- (the other ion is covalently attached to the polymer and is essentially immobile). We then utilize a wide range of complimentary experimental materials characterization tools to understand ion transport, including quasi-elastic neutron scattering and molecular dynamics simulations to study the nanosecond time scales, NMR methods to study longer time scales including the ion diffusion coefficient, dielectric relaxation spectroscopy to understand ion dynamics, linear viscoelastic methods to study polymer dynamics, and ionomer morphology by x-ray scattering and scanning transmission electron microscopy. Incorporation of poly(ethylene oxide) in these polymers plays a vital role, solvating the ions and allowing them to move. We aim to thoroughly understand ion conduction mechanisms in this class of materials, with the ultimate goal of being able to design ionomer membranes with facile transport of small counterions useful in the energy materials arena.

FY 2012 HIGHLIGHTS

The dielectric constant of our Li ionomers (red) decreases as expected by Onsager's model (solid lines), but the Na (blue) and Cs (green) ionomers show a stronger T-dependence of dielectric constant owing to isolated ion pairs aggregating. This aggregation is seen directly in x-ray scattering, as ion aggregation peaks in the 2-4 nm^{-1} wavevector range. This new finding is expected to be a universal feature of ionomers: Ions aggregate as temperature increases because the dielectric constant always decreases, enhancing interactions between ions.

Forces, Crystallization, and Assembly in Nanoparticle Suspensions

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Funding:	$189,591

PROGRAM SCOPE

Our research focuses on understanding the growth, transformations, and assembly of colloidal nanoparticles using a variety of theoretical techniques ranging from first-principles density-functional theory (DFT) to atomic-scale molecular dynamics (MD) simulations. One current thrust is focused on understanding the growth and transformations of titanium dioxide nanoparticles. Here, we are using reactive MD simulations to gain an understanding of nucleation in the anatase-to-rutile transformation, as well as the origins of oriented attachment in the growth and aggregation of colloidal anatase.

A second thrust is aimed elucidating the role of structure-directing molecules in the solution-phase synthesis of Ag and Au nanostructures. In this effort, we are using dispersion-corrected DFT calculations to quantify the interaction of polyvinylpyrrolidone (PVP) with various crystalline facets of Ag and Au to understand why PVP tends to produce Ag nanostructures with {100} facets and Au nanostructures with {111} facets. We are contrasting the structure-directing capabilities of PVP to those of polyethylene oxide (PEO), which is not as successful a PVP in forming Ag nanostructures. We are also studying the role of the solution-phase environment on the structure-directing capabilities of PVP and PEO.

FY 2012 HIGHLIGHTS

We developed a local order parameter for the anatase-to-rutile transformation in titanium dioxide and applied it in long-time MD simulations to understand the nucleation of rutile in anatase nanoparticles and their aggregates. We validated the ReaxFF reactive force field for describing the interaction of water with various surfaces of anatase and rutile, and we performed MD simulations based on the ReaxFF force field to understand the aggregation of anatase nanoparticles in a humid environment. These simulations show, for the first time, that oriented attachment in the growth of nanocrystalline anatase is mediated by surface hydroxyl groups and their recombination to form water.

We used dispersion-corrected DFT, in conjunction with a macroscopic theory, to show that PVP binds more strongly to Ag(100) than it does to Ag(111)—consistent with experimental observations. We showed that the interaction of PVP with these two silver facets is not particularly sensitive to strain, so that PVP should be equally effective for growing strained and unstrained nanostructures. Our calculations indicate that PVP is a better structure-directing agent than PEO for the growth of Ag nanostructures because it binds more strongly than PEO, it shows a greater selectivity for {100} facets, and it is a stiffer polymer, which enhances its {100} binding selectivity. To take into account the solution phase, we fit and validated a force field to describe the interaction of ethylene glycol (solvent) and PEO with Ag surfaces. Studies are underway to fit a similar force field for PVP.

Giant Electrocaloric Effect in Ferroelectric Polymers with Tailored Polar-Nanostructures

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Funding:	$155,000

PROGRAM SCOPE

The goal of this project is to design ferroelectric polymers and related organic dielectrics and tailor their polar-nanostructures to realize large electrocaloric effect (ECE) which can be induced under low electric fields. Electrocaloric effect is the temperature and entropy change of an insulation dielectrics induced by external electric fields. Dielectrics with a large ECE may provide a solution to replace the century-old cooling technology based on mechanical vapor compression cycles (MVCC), which employ strong greenhouse gases. Although ECE has been studied for many decades, the relatively small ECE observed in the past makes it not attractive for practical use. The recent finding in our group of a large ECE, i.e., an adiabatic temperature change $\Delta T > 12\ ^{o}C$ and an isothermal entropy change $\Delta S > 50$ J/kgK, in a class of ferroelectric polymers at temperatures above 50 ^{o}C revives the interests in this field and indicates the promise of developing dielectric materials with giant ECE and other related properties for practical cooling devices which have low energy consumption and are environmental friendly..

FY 2012 HIGHLIGHTS

Employing defects modification to the ferroelectric P(VDF-TrFE) copolymers converts them into the ferroelectric relaxor. The directly measured ECE reveals that the relaxor P(VDF-TrFE-CFE) exhibits a large ECE ($\Delta T > 16\ ^{o}C$) over a broad temperature range (from 0 ^{o}C to 60 ^{o}C). By tuning the P(VDF-TrFE) copolymer composition to 65/35 mol%, additional low temperature phases are introduced, besides the normal ferroelectric and paraelectric phases. As we have shown that the presence of multiple phases in a dielectric material can lead to giant ECE, the experimental study on this copolymer confirms this hypothesis and demonstrates that, by modifying the ferroelectric-paraelectric transition with low dose of high energy electrons, an exceptionally high ECE ($\Delta S \sim 190$ J/kgK and $\Delta T \sim 28\ ^{o}C$) can be achieved in the 65/35 mol% copolymer. Further developing polar-dielectrics for large ECE lead to the study of ECE in liquid crystals (LC). Compared with solid ECE materials, dielectric liquids with large ECE offer many advantages in practical cooling devices. The large ECE discovered in LC 5CB is quite exciting.

Hydrogen Caged in Carbon-Exploration of Novel Carbon-Hydrogen Interactions

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Funding:	$0.00 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

This project seeks to trap hydrogen in carbon nanomaterials via repulsive interactions. Three-dimensional carbon networks that have cages suitable for hydrogen incorporation are targeted for synthesis from unsaturated molecular precursors by means of mechanochemistry. Both dynamic shearing/compression in mechanical mills and static high pressure compression in diamond anvil cells are employed for these mechanochemical syntheses. Unsaturated molecules with appropriate geometries may form three-dimensional networks with cages with geometries suitable for trapping hydrogen. These cages may be also be formed in the presence of hydrogen to trap it during mechanochemical synthesis. Multiwavelength Raman spectroscopy is being used to characterize the mechanochemical syntheses in-situ as the precursors are transformed to networks. First principles materials theory is being used to examine candidate carbon-cage structures suitable for network formation. Repulsive interactions that lead to changes in carbon hybridization that can bind hydrogen are also of interest.

FY 2012 HIGHLIGHTS

We have used Raman spectroscopy to show that high-pressure hydrogen catalytically dissociated by platinum supported on carbon can move to the carbon and form a C-H bond. Formation of this bond is reversible, as removal of the hydrogen leads to the disappearance of the Raman mode characteristic of the bond. The C-H bond energy must be approximately half the energy of the H_2 bond, or such reversibility would not be thermodynamically possible. Poisoning experiments reveal that the catalyst is involved in the reverse path from bonded hydrogen to molecular hydrogen. Our results provide direct microscopic-level evidence for the spillover of hydrogen from platinum to carbon. Hydrogenated C60 has been synthesized, and its ability to trap hydrogen in a network formed upon mechanochemical synthesis is under investigation. The theory of this hydrogenated C60 collapse into a network under mechanochemical conditions is also being investigated.

Chemical Routes to Intermetallic Superconductors

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Funding:	$160,000

PROGRAM SCOPE

The overall goal of this project is to develop chemical synthesis tools that lead to predictable control over composition, structure, and morphology for metal chalcogenide materials that are relevant to superconductivity, solar energy conversion, and energy storage. Secondary goals are to use these chemical tools to discover new solid-state materials, to understand the reaction pathways that lead to their formation, and to learn how to scale up and purify these materials using chemical and biological tools. Toward these goals, we have made the following recent progress. First, we have learned how to synthesize colloidal nanosheets of FeSe, FeS, GeS, GeSe, SnS, and SnSe. Most importantly, we learned that laterally uniform nanosheets of SnSe with tunable thicknesses can be formed through a multi-step nanoparticle coalescence pathway. This insight is opening the door to controlling the morphologies of the other related chalcogenide systems, including their dimensionalities, their sizes, and the facets that are exposed. Second, we developed a new chemical approach for fine-tuning the compositions and phases of these and related metal chalcogenide nanomaterials. This chemistry exploits the strong interaction between a phosphine and a chalcogen (e.g., S, Se), such that the reaction of a chalcogen-rich material with trioctylphosphine causes a controllable amount of the chalcogen to be extracted. This allows us to target specific phases that would otherwise be difficult to access and to purify mixed-phase samples. Third, we discovered and characterized a previously elusive magnetic semiconductor: the tetrahedrally bonded wurtzite polymorph of MnSe, which typically crystallizes in the octahedrally bonded rocksalt structure type. This discovery provides not only a new material, but insights into how chemical techniques typically used for nanoparticle synthesis can also be used to access compounds that are not stable as bulk-scale solids made using traditional equilibrium methods.

FY 2012 HIGHLIGHTS

First, we developed a solvothermal crystallization route to colloidal nanosheets of mackinawite-type FeS, a metastable compound that is of interest for many application areas, including superconductivity. Second, we showed that SnSe nanosheets can serve as templates for the epitaxial nucleation of SnTe, ultimately transforming laterally uniform SnSe nanosheets into laterally uniform SnTe nanosheets with a unique single-crystal nanostructure that incorporates both oriented nanocube protrusions and pores. Third, we reported the synthesis of nanosheet-derived SnS nanoflowers and demonstrated their utility as anodes for Li ion batteries. Fourth, we learned how to modify the synthesis of GeSe nanosheets to produce nanobelts, and we characterized the electrical properties of individual GeSe nanobelts by assembling them across lithographically fabricated microelectrodes. Finally, we published a review article describing recent advances, from our group and others, in the synthesis of colloidal Ge and Ge-chalcogenide nanostructures.

Electric-Loading Enhanced Kinetics in Oxide Ceramics: Pore Migration, Sintering and Grain Growth

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Funding: $200,000

PROGRAM SCOPE

Electrochemical devices are commonly used for energy storage and production, and more are under development for potential future deployment. Many such devices rely on solid electrolytes in which ionic conduction dominates. Examples are solid oxide fuel cells and solid oxide electrolysis cells, which often rely on fast oxygen conduction. This project is intended to investigate possible microstructural changes in such devices under electrochemical forces. The basic idea is that nominally insignificant processes may couple to the large ionic current common in these devices, yielding readily observable non-equilibrium phenomena that substantially alter the microstructure. These phenomena could be especially important in next-generation electrochemical devices, many of which employ nanomaterials in which the characteristic length scale is so short that changes due to non-equilibrium processes may be easily undertaken. Initial studies will focus on yttria-stabilized cubic zirconia, a widely used electrolyte material for solid oxide fuel cells and solid oxide electrolysis cells. Other prominent fast-oxygen oxide ceramics of current interest for oxygen and proton fuel cell applications will also be studied.

FY 2012 HIGHLIGHTS

Our studies focused on yttria-stabilized cubic zirconia, a widely used electrolyte material for solid oxide fuel cells and solid oxide electrolysis cells, have revealed enhanced grain growth at higher temperatures, and pore and gas bubble migration at all temperatures, the latter also leading to enhanced sintering of highly porous ceramics into fully dense ceramics at unprecedentedly low temperatures. These results have shed light on the defect reactions in this ceramic, and demonstrated kinetic processes that fall completely outside the classical paradigm of ceramic sintering/processing. An attendant development is a new in situ thermometry technique that is capable of capturing temperature flashes over one thousand degrees of centigrade.

Optimizing Interaction Potentials to Form Targeted Material Structures

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Funding: $127,000

PROGRAM SCOPE

The goal of this project is to develop a systematic inverse statistical-mechanical methodology to identify interaction potentials in many-body systems of particles that correspond to stable “target” structures.

We will consider a variety of interesting crystal, quasicrystal, liquid, and glassy target structures. Our investigation of the “inverse” problem will lead to a deeper fundamental understanding of the mathematical relationship between the collective structural behavior of many-body systems and the interactions—a basic problem in chemical physics. We are interested in finding the interaction potential, not necessarily pairwise additive or spherically symmetric, that stabilizes a targeted many body system by incorporating structural information that is not limited to the pair correlation function. Unlike previous work, our primary interest is in the possible many-body structures that may be generated, some of which may include interesting but known structures, while others may represent entirely new structural motifs. We believe that this inverse approach holds great promise for controlling self assembly to a degree that surpasses the less-than-optimal path that nature has provided. Indeed, we envision being able to “tailor” potentials that produce varying degrees of disorder, thus extending the traditional idea of self-assembly to incorporate both amorphous and crystalline structures as well as quasicrystals. The notion of tailoring potentials that correspond to targeted structures is motivated by the rich fundamental statistical-mechanical issues and questions offered by this fascinating inverse problem as well as our recent ability to identify structures that have optimal bulk properties or unique thermodynamic, transport, mechanical, and optical properties. Examples of the latter include materials with tailored thermal properties (e.g., zero thermal expansion behavior), elastic constants, optical properties for photonic applications, inverse melting characteristics, and transport properties.

FY 2012 HIGHLIGHTS

The following is a list of the highlights of our accomplishments during last year: (1) discovered novel ground-state crystals with controlled vacancy concentrations and directional interactions; (2) studied inherent structures for stealthy potentials; (3) reconstructed microstructures of heterogeneous materials via stochastic optimization techniques; (4) investigated disordered hyperuniform material systems, including structural glasses; (5) discovered new tessellations of space by elementary polyhedra and applications to crystal structures; and (6) applied percolation theory to understand the setting point of cement pastes.

Integrated Growth and Ultra-Low Temperature Transport Study of the Second Landau Level of the Two-Dimensional Electron Gas

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PROGRAM SCOPE

We are pursuing an integrated growth and experimental study of the two-dimensional electron gas in GaAs in the area of the phase space called the 2nd Landau level. There is mounting theoretical and experimental evidence that several fractional quantum Hall states in this region are not well described by the model of non-interacting composite fermions. For example, the even denominator state at the quantum number 5/2 may result from an unusual pairing mechanism of the composite fermions described by the Pfaffian wavefunction. Moreover, several odd denominator fractional states such as the 2+2/5 and 2+6/13 are quite distinct from their well understood lowest Landau level counterparts.

The goals of this project are to grow high quality samples specially tailored for supporting robust ground states in the second Landau level and to probe these ground states using ultra-low temperature transport techniques. Studies of the dependence on the various growth parameters and the disorder present in the samples are expected to offer insight into the nature of these states and lead to the next generation of improved samples.

FY 2012 HIGHLIGHTS

Since the beginning of our DOE contract, we have produced exciting new data on the reentrant integer quantum Hall states in the second Landau level. We have discovered these states have an unusual anomaly in the longitudinal magnetoresistance. We have associated this anomaly with collective localization and have used it to quantify the onset temperature of these states. We have shown, for the first time, that the onset temperature of these states scales with the Coulomb energy and proven, therefore, the collective nature of the reentrant integer quantum Hall states. We have also made substantial progress in heterostructure design and growth. Our zero-field electron mobility exceeds $20\times10^6 cm^2/Vs$, and we have produced samples that display the largest excitation gap (Δ~570mK) ever measured for the 5/2 fractional quantum Hall state. We also completed a systematic study of the limits to mobility in two-dimensional hole systems. New growth studies initiated this year focus on two primary goals: improving gate stability in nanostructures and systematic exploration of the impact of controlled disorder on fractional quantum Hall states in the 2nd Landau level. This year has also witnessed an expansion of our collaborative efforts beyond Purdue. We now collaborate with DOE-funded researchers at University of Minnesota, Rice University, Sandia National Laboratories, California Institute of Technology, and the National High Magnetic Field Laboratory.

The Dawn of Boron Fullerenes: Key Issues of Stability and Synthetic Routes

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Funding:	$250,000

PROGRAM SCOPE

This project goal is to advance our theoretical understanding of the boron assembly into nanoscale structures, while initiating a series of experimental synthetic trials. Therefore, the planned effort is two-pronged and includes theoretical models and assessment of possible structures and their properties, and experimental work of synthesis and characterization. While embarking into a possibly extensive field, we anticipate including in our scope all three basic possibilities: hollow fullerene-type clusters, boron nanotubes, and mono-atomic boron sheets—analog of graphene monolayer. While theory has predicted some possibility, the actual experimental evidence so far remains rather sparse. This may be due to lack of systematic exploration, or fundamental difficulties yet to be determined. Boron nanostructures, if systematically produced, would open a variety of opportunities. B-fullerenes may lead to a branch of chemistry in a way similar to C60, but with its own and unexpected novelties. Nanotubes should possess electronic properties beneficially more uniform than in the case of carbon, where inherent intermixing of metallic and semi-conducting species remains a serious obstacle for obtaining well characterized material. Recent developments show that a systematic study of stability and theoretical investigation of the basic properties and exploration of possible ways of synthesis for boron fullerenes, tubules, and planar sheets is critically timely.

FY 2012 HIGHLIGHTS

Structural stability and diversity of the elemental boron layers are evaluated by treating them as pseudo-alloy $B_{1\,x}V_x$, where V is a vacancy in the close-packed triangular B lattice. This approach allows for an elegant use of cluster expansion method in combination with first-principles density functional theory calculations, leading to a thorough exploration of the configuration space. A finite range of compositions x is found where the ground state energy is essentially independent on x, uncovering a variety of stable B-layer phases (all metallic) and suggesting the polymorphism, in stark contrast with graphene C or BN. While the experimental realization of 2D boron sheets remains a challenge, it is important to theoretically investigate the possible fabrication methods. Here we explore the formation of B sheets on metal (Cu, Ag, Au) and metal boride (MgB_2, TiB_2) substrates via first-principles calculations. Our results suggest that B sheets can be grown on the Ag(111) or Au(111) surfaces by deposition. B atoms decomposed from precursor, and driven by the gradient of chemical potential, will assemble into 2D clusters and further grow to a larger sheet, while formation of three-dimensional B structures is impeded due to high nucleation barrier.

Fundamentals of Spark-Plasma Sintering: Material Processing for Energy Applications

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Funding:	$190,000

PROGRAM SCOPE

The research 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. SPS is based on the conjoint application of fast heating rates, high axial pressure, and field (electric current-based) assisted sintering. 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.

FY 2012 HIGHLIGHTS

The PI's recently conducted research indicates that the understanding of the material constitutive behavior during SPS is impossible without the analyses of mechanical consolidation, heat transfer, and electric field-induced phenomena at multiple scale levels. 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 newly developed constitutive models of SPS and the interconnected codes at different analysis scales will ultimately lead to the creation of the generic multi-scale framework for modeling of spark-plasma sintering.

The developed concepts will be 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. The porous structure will be an essential element of the design of novel nuclear fuel pellets enabling fission product evolution. 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 SDSU and General Atomics—one of the world's leading resources for the high-technology systems development.

A Fundamental Study of Inorganic Clathrates and other Open-Framework Materials

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Funding:	$130,000

PROGRAM SCOPE

The main goal of this project is to synthesize and investigate the fundamental properties of inorganic clathrates, materials with potential for application in photovoltaics, thermoelectrics, and other energy-related technologies. We apply different synthetic approaches, including two newly developed methods for the crystal growth of these materials, to investigate their intrinsic structural, transport, magnetic, and optical properties in developing fundamental structure-property relationships and expanding the knowledge base of unique properties that arise from these materials. One of the newly developed crystal growth techniques utilizes spark plasma sintering (SPS), a technique well known for powder consolidation and densification, for the synthesis and processing of materials, including single-crystal growth. The intellectual merit of investigating these materials is closely tied with their novel structure and the corresponding physical properties they exhibit. The rich variety of compositional variations in clathrates is ideal in investigating the fundamental properties of group 14 elements in novel crystal structures and bonding schemes. The research will reveal novel properties that can only be uniquely investigated in these materials.

FY 2012 HIGHLIGHTS

Single crystals of type II clathrates Na_xSi_{136} ($0 < x < 24$) were synthesized for the first time. The structural properties as a function of Na were characterized by single-crystal x-ray diffraction, and their electrical and thermal properties as a function of Na content were investigated. Non-metallic behavior was observed for $x < 8$, corroborating the expected metal-to-insulating transition at $x \sim 8$. In addition, selective synthesis of single-crystal and microcrystalline type I clathrate Na_8Si_{46} and type II clathrate $Na_{24}Si_{136}$ was achieved via SPS for the first time. The size of the crystals increased with pressure in the case of $Na_{24}Si_{136}$. Microcrystalline specimens were obtained at 60 MPa, and single-crystal specimens were obtained at 100 MPa, at temperatures of 450°C and 600°C for the type I and II phases, respectively. SPS processing may also have promise for the preparation of nano-crystalline Si, as Si nanocrystals with an average size of 65 nm were synthesized by SPS.

Studies of Surface Reaction Mechanisms in Atomic Layer Deposition

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Funding:	$200,000

PROGRAM SCOPE

This project is aimed at discovering the governing mechanistic principals for atomic layer deposition (ALD). ALD promises to be an enabling technique for creating the innovative nanostructured materials needed for future applications, including those in solar energy and photoelectrocatalysis. A difficulty in developing ALD processes, however, is that molecular-level knowledge of ALD mechanisms is generally not known. The goal of the proposed project is to perform both experimental and theoretical studies aimed at uncovering the molecular level mechanisms active during ALD. A combination of in situ and in vacuo infrared spectroscopy, x-ray photoelectron spectroscopy, synchrotron radiation photoelectron spectroscopy, and x-ray diffraction studies, with density functional theory calculations, are employed. The research focuses on three ALD systems: TiO_2, Pt, and Ru. Studies of the metal systems are intended to allow a framework of governing principals for metal ALD to be developed. The studies will enable us to learn about the relationship between reaction and nucleation mechanisms, to understand the chemistry of different ligands, and to elucidate the role of the substrate in controlling the metal and metal oxide ALD processes as a function of temperature. These studies are also expected to lead to a better understanding of the relationship between nucleation and crystallographic phase of the substrate and the deposited film. The research works toward fundamental advances in the understanding of surface chemistry and materials deposition that will be important to a wide range of applications, including energy-relevant technologies. It supports the DOE objectives of providing the scientific foundation for the ultimate design and synthesis of new materials for applications in energy.

FY 2012 HIGHLIGHTS

We have made progress toward understanding mechanisms in ALD in four key areas. (1) We performed in situ and in vacuo mechanistic studies of Pt and Ru ALD, obtaining some of the first direct, detailed measurements of surface species in the Pt ALD process. (2) We developed a new Ru ALD process and explored the effect of precursor on ALD behavior. (3) We elucidated the effect of substrate phase, organic templating, and surface structure on nucleation in Pt ALD. (4) We initiated x-ray diffraction studies of ALD nucleation and growth at the Stanford Synchrotron Radiation Lightsource.

Novel Theoretical and Experimental Approaches for Understanding and Optimizing Hydrogen-Sorbent Interactions in Metal Organic Framework Materials

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Funding:	$360,000

PROGRAM SCOPE

The aim of this program is to develop a fundamental mechanistic understanding of the interaction of guest molecules (such as H_2, CO_2, N_2, or CH_4) 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 a number of 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 enhance 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. 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 2012 HIGHLIGHTS

We have developed a highly porous MOF (Cu-TDPAT) that is thermally and water stable. Its high-density dual functional sites lead to both high capacity and high selectivity for CO_2 capture and separation under conditions mimicking post-combustion flue gas mixtures. We further performed the first IAST calculation to investigate the effect of water on CO_2 adsorption in a three-component gas mixture (CO_2, N_2, and H_2O). Using a new flexible MOF developed in previous years at Rutgers, RPM3, we discovered an unexpected hydrocarbon selectivity, based on differences in their gate opening pressures. We found selectivity dependence on both chain length and specific framework-gas interaction. Combining Raman spectroscopy and theoretical vdW-DF calculations, we uncovered the separation mechanisms governing this unexpected gate opening behavior. We also investigated the effect of water in another important MOF (i.e., MOF-74), finding that it its presence has a drastic impact on the uptake and selectivity of other gases, with important implications for storage and sequestration applications. And finally, we investigated the diffusion of small molecules in MOF-74 by means of *ab initio* density functional theory, identifying specific diffusion mechanisms and successfully uncovering transport processes, at the atomistic level, that govern the transport processes at the experimentally measured macroscopic level.

Group IV Nanomembranes, Nanoribbons, and Quantum Dots: Processing, Characterization, and Novel Devices

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Funding:	$150,000

PROGRAM SCOPE

This theoretical project will be carried out in close interaction with the experimental project at UW-Madison under the same title led by PI Max Lagally and co-PI Mark Eriksson. Extensive computational studies will be performed to address a broad range of topics from atomic structure, stability, and mechanical property to electronic structure, optoelectronic, and transport properties of various nanoarchitectures in the context of Si and other nanomembranes. These will be done by using combinations of different theoretical and computational approaches, ranging from first-principles calculations and molecular dynamics (MD) simulations to finite-element (FE) analyses and continuum modeling. Specifically, for the atomic, morphological, and mechanical properties, we will focus on the following topics: (1) strain enhanced stability of graphitic phase of zinc-blende semiconductors, (2) self-assembly of Ge QDs on freestanding Si nanomembranes, and (3) nanoarchitecture of III-V strained thin films. For the electronic, optoelectronic, and transport properties, we focus on (1) electronic properties of Si and Ge “strain” superlattices, (2) electronic and optoelectronic properties of Si and Ge “strain” quantum dots, and (3) surface and defect core level shift in strained Si(001).

FY 2012 HIGHLIGHTS

A recent highlight is our discovery of fractal Landau-Level (LL) spectra in twisted bilayer graphene. For a specific range of rotational angles, the twisted bilayer graphene serves as a special system with a fractal energy spectrum under laboratory accessible magnetic field strengths. Their unique feature arises from an intriguing electronic structure induced by the interlayer coupling. Using a recursive tight-binding method, we systematically mapped out the spectra of their LLs as a function of the rotational angle, giving a complete description of LLs in twisted bilayer graphene for both commensurate and incommensurate rotational angles and providing quantitative predictions of magnetic field strengths for observing the fractal spectra in these graphene systems. Our experimental collaborators plan to confirm our theoretical prediction by fabricating the twisted bilayer and multilayer graphene through transfer of graphene sheets onto Si nanomembrane substrates.

High-Throughput Preparation and Characterization of Vapor-deposited Organic Glasses

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Funding: $146,000

A summary for this program was not available at press time.

Atomic Layer Controlled Growth of Pnictide Superconducting Thin Films Heterostructures by Design

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Funding: $100,000

PROGRAM SCOPE

The discovery of superconductivity with transition temperatures of 20-50 K in iron-based materials has initiated a flurry of activity to understand and apply these novel materials. The superconducting mechanism, structural transitions, magnetic behavior above and below T_c, doping dependence, and critical current and flux-pinning behavior have all been recognized as critical to progress toward understanding the pnictides.

A fundamental key to both basic understanding and applications is the growth and control of high-quality epitaxial thin films. The ability to control the orientation, the strain state, defect and pinning site incorporation, the surface and interfaces, and potentially the layering at the atomic scale, are crucial in the study and manipulation of superconducting properties. Our main tasks are to control pnictide thin film and oxide templates at the atomic level to understand the relation between structure and superconducting properties, and to design and grow novel crystalline pnictide heterostructures 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 thin film and superlattice synthesis of pnictide films on oxide templates by pulsed laser deposition with in situ high pressure RHEED, to investigate fundamental superconducting properties of pnictides; (2) strain engineering for control and investigation of superconducting properties; (3) understanding and control of flux-pinning mechanisms, and (4) pnictide grain boundary engineering.

FY 2012 HIGHLIGHTS

We have grown artificially layered superlattice structures in Co-doped Ba-122 thin films with controlled structural and compositional modulations. The insertion of O-Ba-122 layers allows nanoparticle formation that introduces strong vortex pinning along the *ab*-planes while still allowing the formation of vertically-aligned defects. The remarkable enhancement of the pinning properties over a wide angular range related to the *ab*-plane nanoparticles is highlighted by the significant increase of the irreversibility field and by much improved J_c. The engineered structures presented here are surely capable of further refinement by optimizing interlayer separation and the composition of the vortex pinning layers features which cannot be obtained in single layer films. The successful growth of such high quality artificially layered structure will have wide implications for achieving new interface-driven high T_c superconductivity and potential device applications involving SNS and SIS junctions. Furthermore, artificially made multilayer structures can also be used as model systems to study many physical phenomena such as dimensionality, proximity effect, and interface pinning.

Group IV Nanomembranes, Nanoribbons, and Quantum Dots: Processing Characterization, and Novel Devices

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Students:	3 Postdoctoral Fellow(s), 2 Graduate(s), 3 Undergraduate(s)
Funding:	$470,000

PROGRAM SCOPE

Our program addresses a broad spectrum of synthesis, processing, and characterization themes in Group IV semiconductor nanomembranes, a disruptive materials platform. Specifically our interests have focused on (1) strain engineering and the use of strain to modify properties in very thin sheets or ribbons; (2) integration of membranes via transfer, bonding, and growth to create new properties; (3) development and use of tools and methods for novel characterization; (4) theoretical interpretation and prediction via efforts with collaborator Feng Liu (Utah) and theorists locally; and (5) exploring the use of nanomembranes to address grand challenges as envisioned by DOE-BES. Much of this work fits well into the broad vision of mesoscale science, the regime where classical microscale science and nanoscale science meet. We emphasize understanding fundamental physical and chemical phenomena, rather than making devices, with a focus on structure and defects, electronic band structure, electronic and thermal transport, and mechanical behavior vis-à-vis modification of the surfaces, modification of the lattice constants, integration of different materials, and membrane distortion.

FY 2012 HIGHLIGHTS

We have published 10 papers in FY 2012, with another 5 submitted. Among the highlights are (1) investigations of InAs nanostressor growth on free-standing Si nanomembranes, showing novel stress distributions; (2) experimental and theoretical investigation of mechanically straining a Ge nanomembrane biaxially to change the Ge band structure sufficiently to make Ge direct-band-gap, and thus able to emit light; (3) experimental demonstration of biaxial strain and 3D mesoscale structure formation in Si nanomembranes using strain adjustable soft polymer support materials; and (4) theoretical demonstration of new cousins of multilayer graphene in compound form via graphitic thin films stabilized by epitaxial strain.

Surface-Reaction-Limited Pulsed Chemical Vapor Deposition for Growing Nanowires Inside Highly-Confined Spaces

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Funding:	$140,000

PROGRAM SCOPE

The objective of this project is to obtain in-depth understanding of the nanoscale crystal growth behavior in a surface-reaction-limited pulsed chemical vapor deposition process, and thereby achieve well-controlled syntheses of three-dimensional nanowire (NW) arrays inside highly-confined spaces. An experiment-based project is proposed to study the nucleation and anisotropic crystal growth mechanisms of titanium dioxide (TiO2). This understanding will then be applied to controlling the composition and dimensionality of TiO2 NWs and eventually to the growth of other functional materials.

FY 2012 HIGHLIGHTS

This project started on September 1, 2012. From September 1 to September 30, 2012, we began setting up a new atomic layer deposition system that can be operated under high temperature (>600°C) and using solid precursors. Crystal structure of TiO2 nanorods in the early growth stage (<100 cycles) was studied using scanning electron transmission microscopy.

Templated Bottom-up Synthesis of Semiconducting and Nanostructured Graphene Materials

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Funding:	$150,000

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 in confined patterns and channels, controlling the crystallinity of the graphene materials, and learning the mechanisms that determine the 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 2012 HIGHLIGHTS

We have realized the bottom up growth of graphene nanostructures using aluminum oxide barriers on Cu substrates and have shown that the barriers can restrict the nucleation of graphene to the exposed Cu and then guide its growth, remarkably, with 1 nm lateral precision. We have used the technique, in particular, to fabricate single-layered structures including channels, nanoribbon arrays, and nanoperforated membranes, with features as small as 25 nm, over areas as large as 1 cm^2. The materials are highly crystalline with domains > 4 microns and with edge-defect concentrations reduced by a factor of 2-10*x* compared to top-down etched samples from literature. Electrical transport measurements of graphene nanoribbon arrays (width = 25 nm) indicate high mobility (215 $cm^2/V/s$). These results are published in NS Safron et al. Advanced Materials DOI: 10.1002/adma.201104195 (2012).

New Frontiers in III-Nitride Selective Area Growth: Nanoepitaxy and Lateral Evolution

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Funding:	$170,000

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 2012 HIGHLIGHTS

Non-epitaxial formation of single-crystalline GaN on SiO_2 has been demonstrated by combining the concept of evolutionary selection (ES) with selective area growth (SAG). The ES-SAG method lifts the requirement for an epitaxial template to be present for the formation of device quality semiconductor layers. While the methods to demonstrate the achievement of wafer-scale thin film single crystalline materials on amorphous substrates are still elusive, the area achievable with this method, exceeding tens to hundreds of square micrometers, is sufficient for the majority of device applications. In addition, the crystal size and position are precisely controlled by lithography, thus providing a uniquely suitable approach for the heterogeneous integration effort of III-V semiconductors and Si CMOS. The concepts explored here are anticipated to provide universal and flexible integration of semiconductor materials with a new range of substrates, including oxides, metals, ceramics and glass.

DOE National Laboratories

Novel Materials Preparation and Processing Methodologies

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Funding:	$1,632,000

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 focuses on developing synthesis protocols for energy materials that contain volatile, reactive, or toxic components such as the rare earth metals, Mg based alloys, and Fe-As based superconductors. The objective of Novel Materials is to (1) quantify and control processing-structure-property relationships between chemical inhomogeneities and structural defects and properties of highly responsive materials; (2) advance the ability to synthesize and characterize high purity, high quality materials, primarily in single crystal form; and (3) 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 2012 HIGHLIGHTS

Progress in FY 2012 was focused in four areas of synthesis:

(1) Controlled single growth of $K_xFe_{1.6+y}Se_2$ allowed for the determination that phase separation is driven by the iron vacancy order-disorder transition. High quality KFe_2As_2 single crystals were grown with the highest residual resistivity ratio (RRR) using the liquid Sn melt-sealing technique. We collaborate with three groups on the investigations of high pressure, penetration depth, and optical infrared spectra for characterization of KFe_2As_2.

(2) The microstructure of alloy compositions in the Mg_2Si-Si, ranging from the hypo-eutectic to hyper-eutectic, have been mapped, showing the composition close to the eutectic composition gives finest and

more uniform structure. A sealed tantalum crucible method has been found to be suitable for alloy synthesis that prevents Mg loss. Thermoelectric property measurements are underway for the uniform eutectic Mg_2Si-Si microstructure as a function of growth rate.

(3) We investigated production of pure Ni and Sn particulate by spark erosion with common set of parameters (but different dielectric) with Si-Sn alloy electrodes, revealing a comparative increase in nano-particle yield in the lower melting Sn case. Parameter variation studies were conducted to promote control of particulate size, emphasizing the nano-metric range and enhanced uniformity of resulting particle composition, including the effect current densities and electrode polarity, and observed increased erosion homogeneity and apparent yield of nano-metric size.

(4) We completed the acquisition, installation, and commissioning of a high pressure, high temperature gradient Bridgman furnace for growth of novel materials containing volatile components.

Structure and Dynamics of Condensed Systems

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Students:	8 Postdoctoral Fellow(s), 6 Graduate(s), 3 Undergraduate(s)
Funding:	$2,311,000

PROGRAM SCOPE

The research effort proposed here 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 2012 HIGHLIGHTS

New insights are emerging that demonstrate distinct levels of order within the structure of liquids and their glasses. Our rapidly evolving understanding arises from new structural information made possible by studies at the Advanced Photon Source, state-of-the-art electron microscopy and atom probe tomography, and new computational tools. This new method of spatially resolving the true three-dimensional pair distribution function has enabled us to unearth the longer range order in liquids and their glasses. These atomic scale descriptions fit experimental data better than previous means of describing disordered systems which are based on nearest neighbors such as icosahedral-like clusters. The new model shows many crystal-like polyhedra as well as clustering of polyhedra—features not seen in previous models. Longer range structures emerge by linking these smaller, more stable clusters during the undercooling of the liquid. These cross-linking regions appear to be responsible for behaviors such as decreasing diffusion in undercooled liquids and increasing heat capacity. The topology of these stable regions is dependent both on the chemistry and the thermal history of the alloy system and has been demonstrated in both experiments and simulations. We have shown that these variations in disorder can have a profound influence in the phase selection during devitrification of the amorphous alloy or during solidification of a deeply undercooled liquid. We have further shown that solidification pathways are also highly dependent on the liquid structure. A fundamental understanding of these competing structural motifs in the liquid should allow us to develop new processing methods to tailor new materials form old chemistries.

Digital Synthesis - A Pathway to Create and Control Novel States of Condensed Matter

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Funding:	$705,000

PROGRAM SCOPE

Interfaces between complex oxides provide a unique environment where the charge, spin, and lattice degrees of freedom may “reconstruct,” giving rise to novel states of condensed matter. In our research program, we seek to create, explore, understand, and manipulate these states. We use digital synthesis, where we create superlattices and heterostructures by interleaving integer layers of the constituent materials, and all charge transfer or doping takes place at atomically sharp interfaces. We will explore properties of materials that are known to have interesting collective phases, such as the manganites, nickelates, and titanates, where the effects of disorder have been engineered away by digital synthesis. We shall explore two-dimensional Ruddlesden-Popper phases where dimensional confinement gives rise to novel behavior. We seek to create and discover materials that are on the verge of a transition and tune these with external fields and currents. Lastly, we will explore a new class of materials in the 5d transition metal oxides, where strong spin-orbit interactions play a definitive role. This leads to novel correlated insulators and may give rise to superconductors and topologically protected surface states according to theoretical predictions. We will synthesize materials using state-of-the-art, ozone-assisted oxide Molecular Beam Epitaxy at Argonne and characterize them using a comprehensive set of tools, including magnetic and transport measurements, x-ray, and neutron scattering and electron microscopy.

FY 2012 HIGHLIGHTS

We realized a delta-doped ferromagnet in an antiferromagnetic (AF) manganite by adding a single atomic layer of electron dopants to the antiferromagnet. The ferromagnet was shown to form via canting of the AF spins. This was the first direct demonstration of an idea proposed by de Gennes. We exploited this to create a quasi-2D region of ferromagnetism, in a manner that is unique to the mechanism of double exchange ferromagnetism. We also wrote a detailed review of the physics of manganite heterostructures.

Exploratory Materials Synthesis and Characterization

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Funding:	$587,000

PROGRAM SCOPE

Our core research program concentrates on the synthesis and characterization of the new model materials of current interest in condensed matter physics. We place strong emphasis on the discovery of new phenomena associated with correlated electron behavior, superconductivity and magnetism. We currently pursue several interpenetrating research directions: quantum criticality, metal insulator transitions in nearly magnetic materials, bulk materials with Dirac dispersion in the band structure, and facility development such as advances in materials synthesis methods and crystal growth.

FY 2012 HIGHLIGHTS

Crystals made at EMSC BNL enabled several important neutron studies. In heavy fermion superconductor CeCoIn$_5$, a single vortex lattice VL orientation is observed for H↑↑[100], while a 90º reorientation transition is found for H↑↑[110]. The VL form factor shows strong Pauli paramagnetic effects similar to H↑↑[001]. At high fields, above which the upper critical field becomes a first-order transition, an increased disordering of the VL is observed [Phys. Rev. Lett 108, 087002 (2012)]. In addition, spin fluctuations are reported near the magnetic field-driven quantum critical point in YbRh$_2$Si$_2$. On cooling, ferromagnetic fluctuations evolve into incommensurate correlations located at $q_0=\pm(\delta,\delta)$ with $\delta=0.14\pm0.04$ reciprocal lattice units. At low temperatures, an in-plane magnetic field induces a sharp intradoublet resonant excitation at an energy $E_0=g\mu_B\mu_0H$ with $g=3.8\pm0.2$. The intensity is localized at the zone center, indicating precession of spin density extending $\xi=(6\pm2)$Å beyond the *4f* site [Phys. Rev. Lett. 109, 127201 (2012)].

In 2012, we reported two-dimensional (2D) quantum transport in SrMnBi$_2$ and CaMnBi$_2$ single crystals. The linear energy dispersion leads to nonsaturated linear magnetoresistance since all Dirac fermions occupy the lowest Landau level in the quantum limit. The transverse MR exhibits a crossover at a critical field B* from semiclassical weak-field B^2, to the high-field linear-field dependence. With an increase in temperature, the critical field B* increases and the temperature dependence of B* satisfies the quadratic behavior which is attributed to the Landau-level splitting of the linear energy dispersion. The effective magnetoresistant mobility up to $\mu_{MR}\sim3400$ cm^2/Vs is derived. Angular-dependent magnetoresistance and quantum oscillations suggest dominant 2D Fermi surfaces. Our results imply that bulk crystals with Bi square nets can be used to study low-dimensional electronic transport commonly found in 2D materials such as graphene [Phys. Rev. B 84, 220401 (2012) and Phys. Rev. B 85, 041101 (2012)]. Notably, we have discovered large magnetothermopower effect in these materials, attributed to the shift of the chemical potential in the linear bands by magnetic field [Appl. Phys. Lett. 100, 121111 (2012)]. The maximum change of thermopower is about 1600% in 9 T and at 10 K.

Molecular Beam Epitaxy of Complex Materials

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Funding:	$1,600,000

PROGRAM SCOPE

The mechanism of high-temperature superconductivity (HTS) is one of the most important problems in condensed matter physics. Some basic facts—the spin and the charge of free carriers, the nature of superconducting transition, and the effective interaction that causes electron pairing—are still unclear. We are conducting experiments designed to shed new light on these key questions.

Our main tool is a unique atomic-layer-by-layer molecular beam epitaxy (ALL-MBE) system, which we use for digital synthesis of single-crystal films of HTS cuprates, as well as multilayers and superlattices with atomically perfect interfaces. From these, we manufacture HTS tunnel junctions, field-effect devices, and nano-structures. These unmatched devices, in turn, enable novel, incisive experiments.

FY 2012 HIGHLIGHTS

The MBE laboratory, including the clean room, is fully functional and at peak performance. In FY 2012, we performed over 200 synthesis experiments, most of which produced atomically smooth superconducting films. Every film was characterized by RHEED, R(T) and/or (T) measurements and selected ones also by XRD and AFM. Many were patterned into micro- or nano-sized devices and were subject to detailed studies of their physical properties and behavior, resulting in a number of new observations and results. These were reported in 16 research papers, including 4 in *Nature*-family journals (2 published and 2 under review).

Early Career: In-Situ Monitoring of Dynamic Phenomena during Solidification

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Funding: $500,000

PROGRAM SCOPE

A solidification microstructure is the product of the processing path used to create it. Understanding this linkage is vital for structural materials because the solidification microstructure profoundly affects properties and performance. Processing parameters such as thermal gradient and solid-liquid interface velocity affect the interface stability in metallic alloys during solidification, which can result in pattern-forming instabilities that dictate the morphological and microstructure evolution. In-situ characterization techniques are now affording direct interrogation of opaque materials during synthesis and processing. In this project, the unique tools and probes available at National Laboratory User Facilities will be used to see inside and make movies of metallic alloys during melting and solidification. In-situ characterization of these processes will permit the advancement of solidification theory, the development of predictive solidification and microstructure evolution models, and in-process adjustments through feedback systems to dynamically control microstructure evolution to achieve application-tailored properties. These capabilities will enable process-aware manufacturing studies of materials, reducing the time for process development and the time from discovery to deployment through elimination of trial and error, which are critical for the United States to achieve advanced manufacturing initiatives and remain competitive in the global economy.

FY 2012 HIGHLIGHTS

This five-year project was initiated in May 2012. Real-time imaging using x-rays or protons will be used to capture the dynamics of metallic alloy melting and solidification. During Fiscal Year 2012, we prepared metallic alloys and the experimental capabilities needed for a series of experiments at Argonne National Laboratory's Advanced Photon Source in Fiscal Year 2013. Synchrotron x-ray imaging will be used to study solidification growth regimes (planar, cellular, dendritic) that are important for casting technology and single crystal growth. Data visualization and analysis of results from preliminary experiments were also performed in preparation for upcoming publications and conference presentations. The PI of this project presented at the Advanced Manufacturing Workshop at Los Alamos National Laboratory and at the U.S. Department of Energy review of the Shared Research Equipment (ShaRE) National User Facility at Oak Ridge National Laboratory in Fiscal Year 2012. The PI was also awarded a Presidential Early Career Award for Scientists and Engineers (PECASE), in part for some of her early solidification work, which is the highest honor bestowed by the U.S. government on science and engineering professionals in the early stages of their independent research careers. She was nominated by the U.S. Department of Energy and the National Nuclear Security Administration.

Design and Synthesis of Nanomaterials

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Funding:	$473,000

PROGRAM SCOPE

The overarching goal of this proposal is to elucidate the myriad of instabilities, forces, and materials properties that are operative at the nanoscale (time and space) during the assembly of ordered metallic nanoparticles from pseudo 1D and 2D solid/liquid thin metal films. Single element and multi-component nanoparticle ensembles will be synthesized. This knowledge will not only further the scientific understanding of the stability of thin films/coatings supported on surfaces, especially for ultrathin nanoscale thin films, but also provide a means to engage/control stability or instability for more complex multi-scale or hierarchical, substrate-supported structures. In-situ and ex-situ studies will be conducted to determine the nature of the interfacial interaction between metal films and solid substrates and the role this interaction ultimately plays in film stability. This work will explore the subsequent dynamics in both the solid and liquid states using pulsed laser heating implementing time-temperature profiles with nanoscale resolution. Dynamic characterization of film assembly will facilitate directed assembly efforts whereby synthetic, nanoscale perturbations will be imposed on the starting thin films in order to force instability evolution toward an ordered, assembled final nanoparticle array morphology. Molecular dynamics simulations will be used to reveal the relevant materials physics involved in instability evolution and propagation at the nanometer scale. This proposed approach will elucidate mechanisms which will enable the formation of highly ordered nanoparticle arrays, across multiple length scales, with designed and controlled particle shape, composition, and spatial arrangement.

FY 2012 HIGHLIGHTS

Emphasis in FY 2012 was placed on understanding the nature of the solid–liquid interaction during the self-assembly of liquid metals on dielectric substrates. The assembly is driven by the simultaneous interaction of fluid instabilities and physical forces, yet up until now, the role of the physical force has been poorly understood. These studies were conducted with the ultimate goal of assembling highly ordered, solid metallic nanoparticle ensembles on surfaces. Molecular dynamics simulations revealed that physical (i.e., van der Waals type) interactions significantly impact the solid-liquid interaction by dictating the outcome of nanoparticle assembly. The disjoining pressure model, commonly used to capture the physical nature of the liquid metal-solid dielectric substrate interaction, was quantitatively linked to molecular dynamics results paving the way for predictable self and directed assembly across multiple length scales. Leveraging this enhanced understanding of the role of physical forces during assembly, experiments were conducted which demonstrated the simultaneous assembly of both particle and wire morphologies from a single, simple thin film metal aggregate.

Growth Mechanisms and Controlled Synthesis of Nanomaterials

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Funding:	$1,063,000

PROGRAM SCOPE

This project addresses the link between the growth mechanisms and the resulting structures of nanoscale materials. The emphasis is on the development of real-time methods to induce and probe chemical and physical transformations far from thermodynamic equilibrium. The approach relies on combining real-time diagnostic measurements, predictive theoretical methods, and post-growth characterization using imaging, spectroscopy, and atomic-resolution analytical electron microscopy to develop a framework for deterministic synthesis of nanomaterials. Specifically, the project objectives focus on (1) understanding the special role of nonequilibrium growth environments in capturing metastable phases and structures with novel nanoscale properties, (2) determining the reactive intermediates and kinetic pathways driving the formation of particular classes of nanomaterials through the development of real-time measurement techniques, and (3) understanding the atomistic interactions governing the design and synthesis of nanomaterials with specific structure and functionalities through predictive theory and associated experiments.

FY 2012 HIGHLIGHTS

Research efforts in FY 2012 led to significant advances in the understanding of the growth mechanisms of metal oxide nanoparticles and carbon nanostructures important for energy applications. Using atomic resolution electron microscopy, it was shown that titanium oxide synthesized by laser vaporization initially appears in the form of ultrasmall nanoparticles (UNPs) smaller than 2 nm with a structure different from any known bulk phases. Significant progress was made on a coordinated modeling approach, utilizing both force field and *ab initio* methods, to determine the energy stability of possible new nanophases in these UNPs and in metal alloy nanoparticles synthesized by ultrafast laser ablation. The growth of millimeter size single crystal graphene domains was achieved by using hydrogen to control the nucleation and growth kinetics in chemical vapor deposition (CVD) of graphene on Cu. Sub-second duration carbon source gas pulses combined with real-time diagnostics were used in identifying a fast isothermal graphene growth pathway even on metals with high carbon solubility, such as nickel. Pulsed-CVD was also combined with laser interferometry to understand how single-wall carbon nanotubes (SWNTs) grow in coordinated fashion into aligned arrays, and how the flux of gas determines the density and diameters of the nanotubes in the array. For both graphene and SWNTs, the measured growth kinetics indicate that autocatalytic chemical reactions generate intermediate species that serve as “building blocks” to accelerate growth. Using the same concept, the growth of new hybrid nanooysters—encapsulated metal nanoparticle quantum dots in hollow carbon shells—were synthesized using single-wall carbon nanohorns and metal nanoparticles as building blocks in an all solid-state synthesis approach.

Structural Origins of Electrochemical and Mechanical Properties in Pre-Formed Solid Electrolyte Interphases

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Funding:	$651,000

PROGRAM SCOPE

The solid electrolyte interphase (SEI) is an enabling component for advanced electrical energy storage (EES) systems. This program intends to direct the rational design and discovery of new materials for pre-formed SEIs with tailored structures and properties that can be used in a range of battery chemistries. The overall goal of this project is to correlate the electrochemical and mechanical properties of SEIs to their atomic, nanoscale, and dynamic structures. Achieving the overall goal of this project requires that fundamental questions be answered: (1) *How does the atomic structure affect the electronic and ionic conductivities of the SEI?* (2) *How does the nanostructure influence the mechanical strength and ionic and electronic conductivities of the SEI?* (3) *How does the dynamic structure of the SEI affect its electrochemical performance?* Our approach will be to create new materials and interfaces based on insights gained using in situ and ex situ characterization techniques and theoretical calculations to unravel the structural origins of electrochemical and mechanical properties in pre-formed SEIs. To address the fundamental basis of interfacial processes during charge and mass transfer, identified as a critical research need for EES, this effort will initially focus on nanostructured SEIs of lithium thiophosphate super ionic conductors (thio-LISICON) and lithium phosphorous oxynitride (LiPON), i.e., examples of crystalline and amorphous materials, respectively. Understanding and controlling the SEI is critical to the development of the next generation EES, an essential step toward substantial future energy strategy, and of vital importance for the nation's energy independence and security.

FY 2012 HIGHLIGHTS

Our efforts were focused on three tasks. (1) Synthesis of novel solid electrolytes. The nanostructure of nanoporous β-Li_3PS_4 was identified as the key to significant improvement (1000x) of its ionic conductivity. Li_3PS_4 was also identified as the effective protective layer in lithium-sulfur (Li-S) batteries. The formation of Li_3PS_4-based SEI on the surface of metallic lithium is crucial to the improvement of cycling performance of Li-S batteries. (2) Development of in situ neutron scattering techniques for the studies of reaction mechanisms of battery materials. Neutron scattering techniques have been developed for the visualization of battery chemistry and the structural changes which occur during battery cycling. This research gives insight to the phase transformation of materials during battery operation. Neutron scattering has also been used as a tool to guide the synthesis of electrode materials. The studies unravel the reaction mechanism for the synthesis of $LiMn_{1.5}Ni_{0.5}O_4$. (3) Understanding of pre-formed SEIs. We implemented the concept of pre-formed SEIs through the sputtering of a LiPON coating on nanoparticles of $LiMn_{1.5}Ni_{0.5}O_4$. The research elucidates the interfacial structures and the functions of the pre-formed SEIs.

Electronic, Magnetic and Optical Properties of Doped Metal Oxide Epitaxial Films and Interfaces

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Sr. Investigator(s): Droubay, Timothy, Pacific Northwest National Laboratory
Kaspar, Tiffany, Pacific Northwest National Laboratory
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Students: 1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding: $742,000

PROGRAM SCOPE

The broad range of properties exhibited by oxides can be extended through selective doping. Epitaxial film deposition allows a high degree of control over composition, provided adequate process monitoring probes are in place. Here we advance the science of oxide molecular beam epitaxy (MBE), and use this technique, along with off-axis pulsed laser deposition, to synthesize novel doped oxide films, interfaces and superlattices. Our overarching goal is to create in a controlled way and investigate well-characterized oxide film structures, in order to elucidate the effect of different composition profiles and structures on magnetic, electronic, optical and magneto-electronic properties. In addition to a multi-faceted experimental approach, we employ state-of-the-art electronic structure calculations to predict structures, energies, and functional properties for select systems, as well as to assist in interpreting experimental results. This work deepens our fundamental understanding of doped oxides and hastens technological advancements related to oxide film deposition.

FY 2012 HIGHLIGHTS

We have carried out combined experimental and theoretical studies of the $LaCrO_3/SrTiO_3(001)$ and $Cr/SrTiO_3(001)$ heterojunctions, and Ga-doped ZnO on α-$Al_2O_3(0001)$. In the LCO/STO investigation, we traced the evolution of the electronic and geometric structures at the interface as a function of LCO layer thickness. We found that a large built-in potential (~500 meV/unit cell) is present within the polar LCO layer on non-polar STO for small thicknesses which decreases with increasing LCO thickness. This potential varies inversely with the extent of cation intermixing at the interface, which in turn increases with increasing LCO thickness. The interface is not conductive, and theoretical modeling reveals that an internal charge rearrangement within the LCO precludes full-blown electronic reconstruction that would lead to charge transfer to the STO. The Cr/STO interface was found to be Ohmic, rather than rectifying, and exhibits the lowest contact resistance of any metal on STO (~30 mΩ-cm). The contact resistance is low because Cr diffuses into the STO and occupies interstitial sites within the first few atomic planes, effectively metalizing the STO. Ga-doped ZnO deposited in a H_2 ambient and exposed to a Zn beam after deposition exhibits very low resistivity (1.2×10^{-4} Ω-cm) and high carrier concentration (1.46×10^{21} cm^{-3}), due to H-assisted Ga incorporation and elimination of Zn-vacancy acceptors.

We made significant progress in the commissioning of a new, custom-designed oxide MBE system coupled to a state-of-the-art x-ray and ultraviolet photoemission spectroscopy (XPS/UPS) chamber. The MBE chamber includes a highly sensitive three-channel atomic absorption flux measuring spectrometer system for in-situ monitoring and control of metal atomic beams. The photoemission chamber includes monochromatic UV (He I & II) and x-ray (Al K_α) light sources, along with a high-performance electron analyzer for high-energy resolution XPS and UPS, including band mapping.

Molecularly Organized Nanostructured Materials

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Funding:	$660,000

PROGRAM SCOPE

Self-assembled materials with controlled nanostructures and functions have great potential for energy storage and conversion. The overall goal of this project is to investigate molecularly-directed crystallization and self-assembly phenomena at interfaces for synthesizing nanostructured materials with controlled micro- and nanoporosity and desired stable crystalline phases. 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.

FY 2012 HIGHLIGHTS

Functionalized graphene sheets (FGS) as molecular templates for controlled crystallization and self-assembly: Surfactants and polymers directed self-assembly has been successfully used to prepare mesoporous and nanostructured materials. This method is effective for simple one-component systems, but it is difficult to control the crystalline phase and orientation of multicomponent materials. Among the directions of the project are to investigate the fundamental interactions in well-defined 2D graphene sheets and explore new concepts for forming complex 3D systems based on nanoscale building blocks. We demonstrated that FGS is a new class of molecular templates for controlling nucleation and self-assembly of graphene-metal oxide nanocomposites. The interfacial chemistry plays a key role in controlling the nucleation sites and crystalline phases. FGS can also direct the self-assembly of ordered micelle structures and ordered mesoporous nanocomposites. FGS molecular templates provide a good opportunity to prepare novel bulk structured nanocomposite materials in which the template also serves as a key functional component to improve the properties such as electrical conductivity and mechanical stability of energy storage materials. Theoretical simulation and experimental studies reveal that the functional groups on FGS play a key role as nucleation sites for metal oxides. The nucleation of metal oxides (SnO_2, TiO_2) on FGS is energetically favorable on the functional groups, but not so on pristine graphene. In addition to controlling the nucleation sites, FGS can also alter the stability of a specific crystalline phase. We also developed a graphene templated rapid evaporation and self-assembly method to prepare ordered crystalline metal oxides using surfactant micelles as structural directing agents. After the ordered micellar structures are formed with the amorphous metal oxides on FGS during rapid evaporation, the materials can be annealed to achieve desired nanocrystallite phases without destroying the ordered structures. This self-assembly approach is applicable to a range of metal oxides including TiO_2, ZrO_2 and mixed oxides.

Theoretical Condensed Matter Physics

Institutions Receiving Grants

Many-Body Theory of Energy Transport and Conversion at the Nanoscale	
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Funding:	$100,000

PROGRAM SCOPE

This project addresses the fundamental challenge of understanding nanosystems far from equilibrium while simultaneously exploring the potential of nanostructured materials for applications in energy-conversion technologies. The main focus of the project is the study of quantum-enhanced thermoelectrics. The PI and collaborators recently predicted a dramatic enhancement of thermoelectricity on the nanoscale due to quantum wave interference. This project builds upon these ideas by investigating quantum thermoelectric effects in multiterminal geometries—a largely unexplored problem—and by studying the effect of electron-electron interactions on higher-order quantum interference. Fundamental research on the nonequilibrium many-body theory of nanostructures is conducted in parallel, to enable the applied research on nanoscale energy conversion.

FY 2012 HIGHLIGHTS

We developed an effective field theory of interacting π-electrons and used this to describe transmission eigenchannels in single-molecule junctions and to study the effects of electron-electron interactions on higher-order quantum interference. Together with Kieron Burke, Justin Bergfield, and Zhenfei Liu, we developed an exact description of the Anderson impurity model within the Kohn-Sham scheme of density-functional theory. An exact result for the scaling form of the exchange-correlation potential due to the emergence of the derivative discontinuity was obtained.

We derived a general solution of the problem of heat transport in three-terminal thermoelectric devices in the linear-response regime, and used this to formulate a precise definition of—and develop a realistic model of—a quantum electron thermometer with atomic resolution.

Theoretical Investigation of Magnetization Dynamics at Elevated Temperature

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Funding:	$80,000

PROGRAM SCOPE

This scientific program intends to establish a theoretical framework for modeling and predicting magnetization dynamics of magnetic nanosystems at elevated temperatures. Fast magnetization dynamics excited by external perturbations such as laser pumping and high current heating involves physics on the time scale of picoseconds and femtoseconds, several orders of magnitude faster than conventional nanosecond magnetization dynamics in hard disk drive devices. The proposed research consists of two broadly defined objectives. The first is to identify physical processes responsible for the magnetization dynamics by studying the microscopic interactions among conduction electrons, spins, and lattice. The non-equilibrium electrons excited by external sources transfer their energy and angular momenta to both spins and lattice via electron-spin wave interaction and spin-orbit coupling. Near the Curie temperature of spin systems, the dynamics show critical behaviors; and thus it is expected that magnetization dynamics are highly dependent on the detailed distribution of the non-equilibrium states. The second objective is to establish an effective description for ensemble magnetization so that the experimental results can be modeled by an effective dynamic equation. Similar to the conventional Landau-Lifshitz-Gilbert equation which has been widely used for addressing nanosecond magnetization dynamics at low (or room) temperatures, the effective equation developed in this proposal will be useful for the application of picosecond and femtosecond magnetic devices. The program intends to deliver a number of numerical algorithms and codes for applications in various systems.

FY 2012 HIGHLIGHTS

We have made progress in both proposed topics. On the development of an effective dynamic equation for high temperature, we have explicitly constructed the equation based on the quantum kinetic approach. The resulting equation shows rich dynamic behaviors near Curie temperatures. In particular, the interplay between longitudinal and transverse relaxations is revealed. On the microscopic calculation of the laser-induced magnetization dynamics, we have extended the 3-temperature model and found key material parameters that control the time scale of fast magnetization dynamics.

Properties of Multiferroic Nanostructures from First Principles

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Funding:	$150,000

PROGRAM SCOPE

Multiferroics are materials that can simultaneously possess ferroelectricity (that is, a spontaneous electrical polarization that can be switched by applying an electric field) and magnetic ordering. Such class of compounds exhibits a magnetoelectric coupling that is of high technological relevance, since it implies that electrical properties are affected by a magnetic field or, conversely, that magnetic properties can be varied by an electric field.

The broad objectives of this proposal are to gain a deep understanding of multiferroic nanostructures, in general, and to reveal original, exciting phenomena in low-dimensional multiferroics, in particular.

To achieve these objectives, several research projects on multiferroic nanostructures have been conducted (and are currently conducted) by developing and/or using state-of-the-art techniques from first principles. Collaborations with internationally-recognized groups, including DOE scientists, having vital experimental programs in multiferroics are further strengthened, which allow us to ground our simulations and to fully, deeply understand the complex materials under investigation.

FY 2012 HIGHLIGHTS

We discovered several novel phenomena and new structural phases in low-dimensional multiferrocs during FY 2012. We are confident that our results are significantly enhancing the current understanding of multiferroics and nanostructures, by revealing their (anomalous) properties, identifying the microscopic features responsible for such properties, and by discovering new phenomena.

We hope that these insights will have great impacts in designing new and improved devices for, e.g., actuators, sensors, and energy storage. Such devices are important to the DOE missions in energy efficiency and transportation technology.

Disorder and Interaction in Correlated Electron Systems

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Funding:	$150,000

PROGRAM SCOPE

The study of correlated electron materials represents both the challenge and the vitality of condensed matter and materials physics. Due to their remarkable physical and material properties, the transition metal oxides, pnictides, and chalcogenides occupy an especially important place in this field. The goal of our program is to investigate the fundamental effects of electronic correlation and disorder on the emergent quantum electronic states, low energy excitations, and unconventional superconductivity in these materials. Examples include theoretical studies on the nature of the magnetism and the mechanism of superconductivity in Fe-pnictide superconductors; on what controls the large variations in the superconducting transition temperature T_c in the high-T_c cuprate superconductors; and on the origin of the unconventional pseudogap phase that straddles the disparate antiferromagnetic insulator and the *d*-wave superconductor. The program also aims at developing theoretical ideas and methodology for understanding the strong correlation problem, as well as investigating new, emergent phases of matter in strongly correlated electronic systems.

FY 2012 HIGHLIGHTS

We have continued to investigate our proposed mechanism of charge fluctuation mediated superconductivity in Fe-based superconductors, focusing on proposing experimental tests for the theoretical predictions. We have also shown theoretically that a layered superconductor with a full pairing energy gap can be driven into a nodal superconducting state by interlayer pairing when the superconducting state becomes more quasi-three-dimensional, which provides a natural explanation for the observed nodal behavior in a class of iron-based superconductors. Based on this theory, we proposed that an anti-correlated *c*-axis gap modulation on the hole and electron pockets can serve as a test for the symmetry of the pairing gap function.

Realizations of Majorana fermions in solid state materials have attracted a great deal of interests recently in connection to topological order and quantum information processing. We devoted substantial effort to investigate whether and under what conditions, combining nodal superconductivity and magnetism, two common caricatures of strongly correlated electrons materials, can produce a stable topological superconductor. We discovered that, remarkably, when a spin-singlet superconductor with nodal excitations coexists with a noncollinear magnetic order, a topological superconductor is born with a single Majorana bound state in the vortex core, at the stable magnetic defect, and on the edge of the superconductor. We will develop microscopic models and propose suitable materials for theoretical and experimental realizations of such topological magnetic superconductors.

Quantum Nano-Wire Multiconnections

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

PROGRAM SCOPE

The assembly of nanostructured materials, at scales intermediate between those of micron-size and of atomic systems, brings the promise of revolutionary new devices. But at the same time, many fundamental science problems are brought into light, such as how to describe the collective quantum behavior of many electrons when they are confined to geometries at the nanometer scale. One of these problems is how electrons behave at junctions, such as Y-junctions of nanowires. The purpose of this project is to understand the basic principles that pertain to the problems of interconnection of multiple nanowires. Junctions at the nano scale differ in many important ways from their counterparts in the micro and millimeter scale, because of the combined effects of electron-electron interactions and confinement to just a few quantum channels. The goals are to characterize these quantum multi-wire connections by applying analytical methods of quantum impurity problems, to develop new analytical approaches that incorporate recently developed mathematical tools from other branches of physics, and to develop numerical techniques based on finite size scalings that are suggested by the analytical studies.

FY 2012 HIGHLIGHTS

We have successfully developed a numerical tool based on density matrix renormalization group that allows us to extract the universal conductance of junctions of multiple quantum wires. The method is based on a key relationship, derived within the framework of boundary conformal field theory, between the conductance tensor and certain ground state correlation functions. Our results provide a systematic way of studying quantum transport in the presence of strong electron-electron interactions, and should be useful for extracting the transport characteristics of molecular junctions. In 2012 we further developed this tool, benchmarked it on junctions of two wires, and applied it to junctions of three wires. We have also written a pedagogical article for other groups to use this method.

The Physics of Graphene

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Funding: $110,000

PROGRAM SCOPE

Graphene is the only known example of a metallic membrane that combines unique issues of soft and hard condensed matter. It conducts electricity extremely well, better than Copper and Silicon, and, just as a rubber band, it can be deformed reversibly up to 20%. Furthermore, there is a one-to-one correspondence between the applied strain and the electronic structure. As the band structure is modified, so is the phase space for electron-electron interactions. The possibility of studying strongly correlated electronic states in a truly two-dimensional (2D) crystal is a fascinating opportunity for theorists and experimentalists alike. Two dimensions is particularly interesting because of its inherent strong quantum and thermal fluctuations that make many-body states, such as superconductivity, magnetism, and charge density waves, quite different from their 3D counterparts. So far, the effects of correlations in unstrained graphene have been fairly elusive, while theory predicts a variety of interaction effects related to the long-range Coulomb potential acting between the Dirac fermions in graphene. Our main goal is to study the mutual interplay of (strain-induced) anisotropies in the electronic structure and electron correlations, with the hope of unveiling the role of correlations in this 2D material. We expect that the non-Fermi liquid behavior, already present in isotropic graphene, is enhanced in strained graphene. In addition, novel strain-induced correlated electronic phases are possible, such as strongly-anisotropic non-Fermi liquids and dimerized states.

Novel Charge and Spin Fractional Quantum Hall Effects and New Emerging Quantum Phases

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Funding: $110,000

PROGRAM SCOPE

The research in this program involves developing theoretical (numerical) approaches to study the nature of new emerging quantum phases and associated novel transport and topological properties in several electron or boson systems. We focus on a few related topics in strongly correlated systems including (1) the fractional quantum Hall effect (FQHE) in topological bands without a magnetic field, (2) the fractional quantum spin (or pseudospin) Hall effect (FQSHE) in topological bands without breaking time-reversal symmetry, and (3) quantum phase diagrams and quantum phase transitions through interaction engineering in complex systems like strained graphene and optical lattices. Due to the nature of strong correlations in all these systems, there is no well-defined analytical theory that can predict the quantum phases for realistic Hamiltonians involving competing interactions. We develop state-of-the-art numerical approaches including exact diagonalization and density matrix renormalization group codes, which can access the ground state and low energy spectrum of different systems containing a large number of particles. At the same time, we design new measurements targeting the nature of the quantum phases, including topological and transport properties, and work closely with other groups who develop analytic theory for such systems. By such joint effort, we make rigorous progress towards a better understanding of the topological matter and the emerging new quantum phases in strongly correlated systems.

FY 2012 HIGHLIGHTS

We have identified novel fractionalized topological phases in flatband models without a magnetic field. We further revealed that strained graphene can host such quantum phases through tuning interactions. We have also shown the quantum phase diagram for Z2 topological insulator in the presence of time-reversal symmetry breaking perturbation. In the next period, we will explore new quantum phases in flatband models with high Chern index and multi-layer graphene systems.

High Performance First-Principles Molecular Dynamics for Predictive Theory and Modeling

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Funding:	$659,000

PROGRAM SCOPE

This project aims at developing a high-performance software infrastructure that combines large-scale first-principles molecular dynamics (FPMD) simulations with on-the-fly computation of vibrational spectra and electronic excitations. This will provide a powerful predictive simulation tool enabling 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 involving breaking and formation of bonds. The software infrastructure will be made available to the research community in open-source form and will accelerate the process of discovery and tuning of new materials properties. It will be connected to other Basic Energy Sciences research by contributing to the interpretation of experimental results obtained at DOE user facilities such as ANL's Advanced Photon Source, ORNL's Spallation Neutron Source, and the Nanoscale Science Research Centers.

Simulating complex systems that accurately represent realistic experimental conditions incurs a high computational cost, which in turn requires an advanced high-performance implementation capable of running efficiently on large parallel computers. The design and implementation of efficient simulation software also face the challenge of the rapidly evolving architecture of new supercomputers. This situation calls for a flexible software design that allows for agile adaptation to new parallel architectures. Our software development will be based on Qbox, a C++/MPI/OpenMP FPMD simulation code developed and distributed by the PI. Qbox is based on Density Functional Theory and has demonstrated excellent scalability on several large parallel platforms including ANL's BlueGene/P and NERSC's Cray XE6 computers. Its object-oriented architecture and use of modern standards (C++, MPI, OpenMP and XML) will facilitate the development and integration of the new features proposed here.

New algorithms and subspace data compression techniques will be developed and used to further accelerate FPMD simulations.

New algorithms recently developed in the Galli group at UC Davis will be used to implement the GW approximation of quasiparticle self-energies and the Bethe-Salpeter equation describing electron-hole excitations. A scalable implementation of Density Functional Perturbation Theory for the computation of the time-dependent polarizability tensor will enable on-the-fly simulation of Raman spectra and give access to, for example, vibrational surface spectroscopy data.

Funding reported is for all institutions.

Semiconductor Nanostructures by Scientific Design

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Funding: $235,000

PROGRAM SCOPE

The goals of this project are to develop and use microscopic simulation techniques to understand and predict materials properties for energy applications; we focus on opto-electronic and heat transport properties for solar and thermoelectric applications, respectively. We aim to provide a first principles description of integrated systems, inclusive of surfaces and interfaces at the nanoscale, and to model realistic environments, directly comparable with experimental conditions.

FY 2012 HIGHLIGHTS

We have developed methods to carry out computational spectroscopy from first principles, and we have applied a combination of these methods and *ab initio* molecular dynamics to the study of semiconducting nanoparticles. In the case of Si nanoparticles, we have discovered (1) how core structures influence electronic gaps and absorption and (2) the role of embedding media on the particle opto-electronic properties. An investigation of the interface between Si nanoparticles and an oxide matrix suggests that the matrix density and the interfacial strain may be used to tune the electronic properties of the nanoparticles (NP), in addition to the NP size [Phys.Rev.Lett. 107, 206805 (2011)].

Theory of Oxide Nanostructures: Polarity, Dimensionality, and Strong Interactions

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Funding:	$110,000

PROGRAM SCOPE

Artificial growth of oxide nanostructures molecular beam epitaxy by pulsed laser deposition has produced several unexpected phenomena, based on a two-dimensional (2D) electron gas (2DEG) between oxides that are insulating in the bulk. At low temperature, both superconductivity and magnetism are observed, and manipulation of the conducting behavior can be carried out with a scanning tunneling microscope tip. We apply density functional methods to examine the atomic-level mechanisms that underlie such phenomena. In nanoscale VO_2 slabs encased within TiO_2 where there is no polar behavior, we discovered a 2D point Fermi surface system that is more peculiar than that of graphene, because charge carriers are massive along one direction but are massive along the perpendicular direction. We also studied naturally nanoscale-layered nickelates such as $La_4Ni_3O_8$, which is insulating in spite of the nominal valences of the ions not summing to zero. Our studies of the $LaAlO_3$ on $SrTiO_3$ interface system were extended to predict the effects of metallic contact layers on the surface, finding that the results are highly dependent of the choice of metal, thus enabling tuning of behavior.

FY 2012 HIGHLIGHTS

While characterizing (theoretically) the paradigmatic charge-ordering transition $2Ni^{3+} \rightarrow Ni^{2+} + Ni^{4+}$ in perovskite nickelates (vi. $YNiO_3$) that occurs in the 300-600 K range and has been probed extensively by experiment, we formulated a means to compare 3D occupancies and discovered that the two disproportionated Ni sites in the broken symmetry phase in fact show no difference in 3D occupation: there is no charge transfer between the Ni sites. We subsequently found that different charge state transition metal ions contained identical 3D occupations in $CaFeO_3$, $AgNiO_2$, and V_3O_4. Similarly, the dformal charge states Cu(2+) and Cu(1+) in the double perovskite, candidate half metallic antiferromagnet, La_2VCuO_6 have precisely the same 3D occupation. Although it has been understood that different charge states can differ rather little in actual charge, our finding means that several metal-insulator transitions (such as the nickelates) now have no explanation. This work had some of its foundation in our work on $La_4Ni_3O_8$, where the natural way for this mixed valent oxide to become Mott insulating (as observed) is to charge order: 3Ni → 2Ni(+) + Ni(2+), but this result could not be obtained in calculations. We achieved a coherent explanation of observations that the Mott mechanism is operating but that it operates on molecular Ni trimer orbitals rather than the atomic orbitals that this mechanism normally requires. We plan to take this research to the next level by (1) identifying absolute 3D and perhaps 2D occupancies (we have focused on differences so far) and (2) reinterpreting “charge ordering” transitions that involve no ordering of charge.

Electron Probes of Nanoscale and Subnanoscale Structures and their Dynamics

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Funding:	$105,000

PROGRAM SCOPE

One main goal of this program is to understand the spin dynamics and the pure spin current propagation in metallic multilayer systems. The ability to control this angular momentum flow without a net charge current presents new perspectives for the detection, transmission, and storage of information in magnetic systems, and opens possibilities to develop new devices with large sensibility, low energy consumption, and high processing speeds. A second goal is to obtain the eigenfrequencies and eigenmodes of dipole-exchange modes of nano wires of rectangular cross section (specifically long wavelength modes along the axis of the wire).

FY 2012 HIGHLIGHTS

Since the original principal investigator, Douglas Mills, passed away, the project is being completed with the help of two of Mills' close collaborators, Filipe Guimaraes and Rodrigo Arias, who have continued their previously planned visits to UC Irvine and have continued collaboration with several experimentalists.

First Principles Investigations for Magnetic Properties of Innovative Materials

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Funding:	$95,000

PROGRAM SCOPE

The goal of this project is to understand magnetic properties of innovative materials, such as magnetic thin films, magnetic semiconductors, d0 magnets, graphene, and topological insulators, by developing and using theoretical approaches based on the density functional theory. Manipulating strength and orientation of magnetization of different systems is probably one of the most active research subjects in condensed matter physics and materials science nowadays. We have performed extensive density functional simulations to investigate electronic, magnetic and transport properties semiconductors, oxides, nanowires, and thin films. Our results are useful for the explanation of experimental data and for the development of new material systems.

FY 2012 HIGHLIGHTS

We introduced a new framework for engineering a two-dimensional spin-orbit coupling gap with impurity bands arising from 5d adatoms through graphene. First principles calculations predict that the gaps generated by this means exceed 200 meV over a broad range of adatom coverage; moreover, tuning of the Fermi level is not required to enter the TI state. The mechanism is rather general and may open the door to designing new TI phases in many materials. The calculated band structures of several graphene systems show that they may have a large topological band gaps. The effects of external electric field and co-adsorption of Cu are also given.

We investigated the mechanism of the substrate-induced spin reorientation transition in FePc/O-Cu(110) and explained the experimental observation in terms of charge transfer and rearrangement of Fe-d orbitals. We found giant magnetoelectric effects in this system, manifested by the sensitive dependences of its magnetic moment and magnetic anisotropy energy on external electric field. In particular, the direction of magnetization of FePc/O-Cu(110) is switchable between in-plane and perpendicular axes, simply by applying an external electric field of 0.5 eV/Å along the surface normal.

Fundamental Theory of Electronic Structure in the Nanoregime: Transport through Single Molecules

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Funding:	$165,000

PROGRAM SCOPE

Creating single-molecule transistor technology is a major thrust of the National Nanoinitiative, and experiments to build and measure the I-V characteristics of such devices continue, enhanced by interest in novel materials such as graphene. There has been a concomitant effort in theory, including *ab initio* electronic structure. The natural language to study transport is Keldysh-Baym non-equilibrium Green's functions (NEGF), especially when many-body effects are important. But only very efficient methods, such as density functional theory (DFT), can produce routine, chemically realistic calculations. Essential questions remain concerning the reliability and accuracy of such calculations for transport.

We will use the fundamental insight and algorithmic development of the previous period to create new, reliable methods for calculating transport. A simple approximate implementation of the standard GW method should be inexpensive and account for the well-known level alignment problems of standard DFT calculations. This method, combined with our complex band-structure algorithm, should also help answer the question of missing XC corrections to the Landauer-Buttiker formula applied to ground-state Kohn-Sham density functional theory. The open-systems density functional theory will be further explored, and a stripped-down (tight-binding) master equation implemented, for studying large systems and general phenomena, such as the crossover between ballistic and diffusive scattering, and transport in solution. Various other fundamental questions, such as the applicability and reliability of time-dependent DFT to transport, will also be addressed.

FY 2012 HIGHLIGHTS

We performed a careful case study of Anderson junction, using NEGF approach combined with DFT. We showed for this system the exact Kohn-Sham functional produces exact conductance for all correlation strengths, at zero temperature and in the linear response regime. Especially, we found in the strongly-correlated limit the exact functional reproduces the Kondo effect, a many-body effect that most mean-field approaches fail to describe correctly. The exact functional can be derived by inverting the Kohn-Sham equation, with occupation calculated by Bethe ansatz. For this system, all errors in conductance come from the approximations of Kohn-Sham functionals. We examined the successes and failures of different functionals, and identified the important features that functionals must have in order to produce accurate conductance. In particular, we found in the strongly-correlated regime, derivative discontinuity must be built in to the approximate functional in order to get meaningful results in this regime.

We investigated 1D continuum systems with long-range interactions, discovering that they mimic 3D systems in many respects [PCCP]. Using the density matrix renormalization group, we computed highly accurate wavefunctions and densities, and determined the KS orbitals and energy components using an inversion algorithm.

Spin-Mediated Energy Transport and Dynamics in Quantum Magnets

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Funding:	$110,000

PROGRAM SCOPE

The focus of this proposal is on theoretical understanding of thermal transport and dynamical properties of quantum magnets, which comprise a diverse class of materials demonstrating a remarkably broad spectrum of complex quantum-mechanical phenomena. There are many fundamental issues related to this interest, such as the problem of ballistic transport in one-dimensional systems. Recent experimental discovery of unprecedentedly large thermal conductivity in spin-chain compounds requires new insight into their properties and new theoretical developments in transport theory as well. Other remarkable effects, such as significant increase of thermal conductivity by magnetic field in a variety of other systems, could open a new window into their fundamental properties and lead to new applications.

Within this proposal, a theoretical understanding is being developed of the energy transport phenomena and dynamical properties of quantum magnets in general and, specifically, of the BEC-like, low-dimensional, and frustrated spin systems. To account for the energy current mediated by the spin excitations, transport theory is used together with the diagrammatic treatment of the scattering processes from microscopic models. If carried to completion, this effort will result in a new and deeper understanding of a large group of materials and can be expected to yield predictions of significant new phenomena.

FY 2012 HIGHLIGHTS

We have made progress in several important areas, such as high-field magnon dynamics, spontaneous magnon decays, and disorder-induced lifetime of gapped excitations in a wide class of antiferromagnets. We have also investigated threshold effects in yttrium-iron garnet, which have a wide-range of implications to the area of spintronics, and studied the role of interactions in the roton energy in 4He, the subject of interest for a wide variety of Bose-condensed systems and ultracold Bose gases.

Strong Correlation, DMRG, and DFT

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Funding:	$330,000

PROGRAM SCOPE

Moderately and strongly correlated materials are at the heart of many energy-related technologies. These materials pose tremendous challenges for modern electronic structure calculation methods. Computationally inexpensive methods, such as density functional theory (DFT), work well for weakly-correlated systems, but typically fail qualitatively when correlation is moderate or strong. Many of the same shortcomings of DFT arise in the context of quantum chemistry when correlations are strong; and molecules, which are weakly correlated at equilibrium, are often very strongly correlated when bonds break during chemical reactions.

Our multipronged approach will advance the state of the art in *ab initio* calculations for electronic structure, both for materials and molecules, encompassing two of the most powerful (and complementary) approaches—DFT and the density matrix renormalization group (DMRG). Key parts of this effort are (1) improvement of approximate functionals by developing an exact framework where new approximations can be tested easily and rapidly; (2) improvement of DMRG methods for very strongly correlated molecules, introducing techniques recently developed in condensed matter physics into quantum chemistry; and (3) the integration of DFT and DMRG to treat large systems with strongly correlated subsystems. The first part is already well under way; the second two are just beginning.

FY 2012 HIGHLIGHTS

This project started during the last quarter of 2012. During that time, we investigated the convergence of DFT when an exact functional is used, where the exact functional is implemented as an algorithm using DMRG. We also investigated the construction of lattice models utilizing the exact Green's function to construct a novel form of Wannier functions.

Density Functional Theory for Phase-Ordering Transitions

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Funding: $140,000

PROGRAM SCOPE

The proposed research aims to develop a new, unifying approach to describe colloidal dynamics and the kinetics of phase-ordering transitions based on accomplishments from previous work for the equilibrium properties of both uniform and inhomogeneous systems and on novel concepts from the state-of-the-art dynamic density functional theory. In addition to theoretical developments, computational research is designed to address a number of fundamental questions on phase-ordering transitions in colloids, in particular those pertinent to a competition of the dynamic pathways leading to various mesoscopic structures, off-equilibrium states, and crystalline phases.

FY 2012 HIGHLIGHTS

Over the past 12 months, the research mainly focused on (1) application of density functional theory to local-and-key interactions in colloidal systems, (2) solvent receding and drying transition near colloidal surfaces, (3) development of an efficient computational procedure to calculate direct correlation function of molecular solvents, and (4) development of theoretical method for rapid prediction of solvation free energy.

Time-Dependent Current Density-Functional Theory of Charge, Energy and Spin Transport in Nanoscale Conductors

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Funding: $105,000

PROGRAM SCOPE

The goals and objectives of the proposed research activities are the study of non-equilibrium phenomena associated with charge, energy, and spin transport in nanoscale systems. The goal is to develop a formulation of the transport problem using Time-Dependent Current Density-Functional Theory (TD-CDFT) and its recent derivatives and generalizations: the quantum continuum mechanics and the stochastic TD-CDFT for open quantum systems. TD-CDFT is the natural framework in which this complex problem can be approached while keeping the solution to a computationally accessible level. This formulation offers several advantages: (1) It directly yields the current that flows in a conductor in response to an arbitrary time-dependent perturbation (including, as a special case, the d.c. current response to time-independent voltages). (2) Because of the dissipative character of the retarded exchange-correlation field, TD-CDFT naturally includes inelastic electron-electron effects, which are inaccessible in the conventional static formulation. (3) Its generalization to open quantum systems allows us to calculate (in principle) the exact ensemble-averaged current density in the presence of energy dissipation and dephasing. In particular, it allows the calculation of dynamical properties driven by the coupling with one or more external environments.

FY 2012 HIGHLIGHTS

We have studied the formation of steady states with and without interactions. We have shown that the particle statistics is important in determining the existence of a finite-current steady state in the thermodynamic limit. In particular, while non-interacting fermions do form a steady state of finite current immediately after the bias is switched on, bosons do not. We have also shown that the local switch-on of interactions on one side of the junction acts as a bias, thus leading to a steady state for fermions. These predictions can be readily verified using atomic gases in optical lattices, where the interactions among atoms can be modulated both globally and locally via optical means.

Computational Studies of Hydrogen Interactions with Storage Materials

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Funding:	$140,000

PROGRAM SCOPE

We use state-of-the-art electronic structure calculations to study the kinetics of hydrogen uptake and release in high-capacity hydrogen storage materials. Our goals are to provide interpretations for experimental observations and to contribute to the design of better storage materials. Mass transport requires formation and migration of point defects in the host material, which we study by first-principles calculations based on density functional theory. For greater accuracy, we have used a hybrid functional approach, which provides improved descriptions of the electronic structure.

Our approach takes into account that defects and impurities in non-metallic systems can occur in charge states other than the neutral state; this important aspect of the problem had previously been overlooked. However, our investigations have shown that this has important consequences for kinetics, and can explain phenomena such as the increase in release rates upon addition of dopants. We have applied the methodology to a variety of materials, including alanates, amides, and borohydrides.

FY 2012 HIGHLIGHTS

We have made significant progress in two areas: dehydrogenation of lithium amide/imide, and decomposition kinetics of aluminum hydride. In both cases, the impact goes well beyond the relevance for the particular material studied. For $LiNH_2/Li_2NH$, we elucidated the underlying mechanisms for particle-size dependence of activation energies for decomposition. The fundamental insights provided here are applicable to the many cases where micro- or nanosized particles are used to enhance reaction kinetics. In the case of AlH_3, we showed that formation of vacancies is the rate-limiting step in dehydrogenation, and demonstrated—based on Kinetic Monte Carlo simulations—that S-shaped reaction curves can occur even when the reaction is diffusion limited. An S-shaped onset of those curves has traditionally been interpreted as ruling out diffusion-limited mechanisms, and our study shows that caution should be exercised when using simple rules about curve shapes to infer reaction mechanisms.

Resolving Frustration in Complex Materials/Interplay of Electron Correlations and Spin-Orbit Coupling

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Funding: $90,000

PROGRAM SCOPE

This goal of this project is to understand the combined effects of the Coulomb repulsion between charges and relativistic spin-orbit coupling. This occurs in materials with heavy 4d or 5d transition metal or 4f lanthanide atoms. Coulomb repulsion, without spin-orbit coupling, is responsible for “electron correlation” effects, which are behind the Mott metal-insulator transition, magnetism, charge ordering, unconventional superconductivity, and other heavily studied phenomena in materials physics. Strong spin-orbit coupling is behind the recently discovered topological insulators, which support novel conducting surface states and unusual magneto-electric effects. Materials with both strong spin-orbit coupling and electron correlation are only just beginning to be systematically investigated experimentally. We expect spin-orbit to fundamentally modify many strong correlation phenomena and support unusual electronic states. Our theoretical research will predict and describe new phases such as “topological Mott insulators” and “quantum spin liquids” in specific materials, describe novel excitations of correlated spin-orbit systems, which are measured for example in resonant inelastic x-ray and neutron scattering, and develop new theoretical techniques. Theoretical models and methods will be carried out in close connection with relevant experiments.

FY 2012 HIGHLIGHTS

We developed theoretical models and analyzed two classes of materials: insulating magnetic double perovskites and quantum pyrochlores. The double perovskites we considered have the formula $A_2BB'O_6$, in which the B ions only are magnetic heavy 4d and 5d elements, and form a frustrated face centered cubic lattice. This structure reduces the orbital overlap of B ions, allowing a relative enhancement of spin-orbit coupling. We derived effective models for these materials, and predicted unusual ferromagnetic, antiferromagnetic, multi-polar ordered, and spin liquid states. Our predictions are being pursued by several experimental groups. In the quantum pyrochlores, we proved the applicability of a minimal 4-parameter model for many rare earth materials of the form $A_2B_2O_7$, where R is a magnetic 4f element, and B is inert. By extensive comparison to neutron scattering data, we derived these parameters for the examples $Yb_2Ti_2O_7$ and $Er_2Ti_2O_7$. We developed a new analytical method to study the ground states and excitations of the minimal model, using techniques borrowed from lattice gauge theory. This method predicts the existence of exotic quantum spin liquid phases, close to the parameters we obtained for $Yb_2Ti_2O_7$. In $Er_2Ti_2O_7$, we instead found an antiferromagnetic ground state stabilized by quantum fluctuations, providing the first irrefutable example of the phenomena of “order by disorder”, predicted decades earlier, in a real material.

Theoretical Studies in Very Strongly Correlated Matter

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Funding:	$230,000

PROGRAM SCOPE

The goal of this project is to develop new techniques for calculating the physical properties of very strongly correlated matter, as relevant for several systems of current interest such as the cuprate superconductors, sodium cobaltate materials, and possibly also heavy Fermi systems. These systems are plagued by the problem of a large repulsive energy scale in the problem that defeats the usual perturbation methods based on Feynman diagrams. Transport properties such as thermoelectric effects are particularly influenced by correlations, and these are of great interest in the project. Also of great interest are the many body properties of the underlying normal state in the cuprate superconductors, with its atypical resistivity and surprising dynamical features such as asymmetric line shapes seen in Angle Resolved Photoemission Studies (ARPES).

FY 2012 HIGHLIGHTS

The work done in this year has developed further a recent and rather involved method found by the PI for dealing with correlations in the extreme limit, i.e., with infinite U so that double occupancy is eliminated. Models such as the tJ model have been proposed and studied by simpler techniques in the past, but the new methodology gives more detailed information about the dynamics of these models in a regime termed the extremely correlated Fermi liquid (ECFL) phase. The Schwinger method of sources has been adapted to give an essentially exact reformulation of the problem as an expansion in the density of particles so that the case of overdoped holes is now accessible. With further effort, the expansion may be pushed to higher orders in particle density so that one can move towards the optimal doping regime that is of great interest. Our group of students and postdocs has taken several pieces of this program and found results of interest that are either published or in the process of publication. A Physical Review Letter has appeared with detailed predictions regarding the low energy asymmetry of the spectral lines in ARPES and also some unusual signatures of extreme correlations that might be visible in tunneling experiments.

We have also started a program of studying the connection of these ideas with other established techniques within this period, such as high temperature expansions for the Greens functions and the expansion around large dimensions in the so called Dynamical Mean Field theory.

Toward High-Accuracy Point Defect Calculations in Materials

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PROGRAM SCOPE

At present, the main limitations for the study of point defects in solids are (1) the inaccuracies resulting from the local density approximation on the band gaps of the host material and on the defect wave function localization because of the self-interaction error, and (2) the effects of finite size supercells. Our goal is to develop improved efficient methodologies to overcome both of these problems.

The approach we are taking to solving the problem is based on the quasiparticle self-consistent (QS)-GW approach. This method provides a static non-local exchange correlation potential extracted from the GW self-energy for which the Kohn-Sham eigenvalues coincide with the quasiparticle excitation energies. The key to making this method applicable to large unit cells required for accurate representation of point defects is that, with a localized basis set, such as the linearized muffin-tin orbitals, the exchange correlation potential can be represented in real space in terms of a LDA+U type ansatz, involving the density matrix and screened Coulomb U and exchange J matrices. If these matrices are found to be sufficiently transferable when restricted to on-site terms, then they can be applied to the defect supercell without much additional computational cost and still incorporate all host band gap corrections as well as orbital dependent self-interaction corrections related to changes in the density matrix.

FY 2012 HIGHLIGHTS

The project started in September 2012. The PI was on sabbatical at the Forschungszentrum Jülich, Peter Grünberg Institute from July 2012 to December 2012, with support from a Fulbright grant. During this time he had a chance to interact with scientist from Stefan Blügel's group who have developed hybrid functional and GW quasiparticle methods based on the mixed product basis set methods and LAPW that are also applicable to the LMTO method. He also discussed and learned about KKR-based Green's function methodologies for point defects developed in the group of Peter Dederichs, Rudolf Zeller, and Phivos Mavropoulos. These studies are useful as preliminary to developing related approaches in the muffin-tin orbital approach as planned under the grant. The PI performed calculations for N in ZnO in the form of molecular N_2 and discovered that, when N_2 is located on a Zn site, it behaves as a shallow double acceptor and can at the same time explain an electron paramagnetic resonance center known in literature when singly occupied. This was established through a calculation of the g-factor. This work has important consequences for the prospects of p-type doping of ZnO, a long-standing unsolved problem. A paper on this work was submitted for publication. Meanwhile, a graduate student working on the project, started calculations at the LDA level for point defects in $ZnGeN_2$, a material targeted for its expected interesting defect properties.

Theoretical and Computational Studies of Functional Nanoalloys and other Nanomaterials

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Funding:	$125,000

PROGRAM SCOPE

Recognizing that nanoalloys are advanced materials of immense scientific and technological interest, our work focuses on understanding structure-function relationship to enable the long-term goal of rational design of functional nanomaterials. Our interest is in understanding factors that control the magnetic and optical properties of these materials. For this purpose, we develop and apply appropriate techniques which require more accurate description of excited and bound states and other correlation effects than afforded by density functional theory (DFT). To ensure dynamic stability of nanostructures, we also determine their vibrational dynamics and thermodynamics. Additionally, we probe non-equilibrium behavior of nanosystems, as in the presence of external fields. Through systematic study of characteristics of selected materials and corroboration of their results with experimental data, we formulate rules and guidelines for predictive material design. The research stages include determination of (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; (3) magnetic properties via our nano-DFT+DMFT approach; and (4) optical response, using time dependent density functional theory and its density matrix version as proposed by us for systems with bound states, multiple excitation, and strong correlation effects. We also intend to develop a non-equilibrium nano DFT+DMFT for extracting non-equilibrium behavior of systems.

FY 2012 HIGHLIGHTS

Application of our recently developed the Nano DFT + nonhomogeneous DMFT method to examine the magnetic properties of sub-nm Fe and FePt nanoparticles (NPs) shows that inclusion of dynamical effects leads to a reduction of NP magnetization and better agreement with experiments (where available) than the DFT+U approach.

We find interesting changes in the optical properties of small Au chains when doped by transition metal (Ni, Fe, Rh) atoms. The plasmon peak of the gold chains (~0.6 eV) splits when doped with Ni/Fe/Pd atoms. We find that the additional peak is associated with a local plasmonic mode which corresponds to charge oscillations around the potential minimum related to the d-orbital states of the impurity atoms.

Using *ab initio* methods, we relate the enhanced low- and high-energy tails n the vibrational density of state of small (< 1 nm) AgCu, PtFe, and Cu NPs to the radial breathing and non-radial tidal vibrations, analogous to the pulsations observed in variable stars. Additionally, we show that the features in the high frequency end can help identify whether a nanoparticles has core-shell or bulk-like structure.

Studies of the Marginally Jammed Solid

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Funding: $125,000

PROGRAM SCOPE

A perfect crystal is the essence of order; in a well-defined way, a collection of spheres at the jamming transition is the epitome of disorder. Our work has shown that this jamming transition is singular in that there is a diverging length scale that appears at the transition. This length scale is due to the fact that the number of inter-particle contacts at the transition is exactly the minimum number needed for mechanical stability. This singularity controls the harmonic as well as the anharmonic properties of the solid in the vicinity of the transition. Our project addresses the following questions: (1) *How does the system behave when pushed beyond the harmonic regime so that anharmonic effects become important?* We have shown that the most anharmonic vibrational normal modes are at low-frequency where they are quasi-localized. These modes are exquisitely sensitive to stress or temperature because they have low energy barriers to particle rearrangements. *Can these modes be used to predict where local failure might occur?* At the jamming transition, anharmonic effects diverge. *How do they evolve as the system is compressed above that transition? Can we predict from the anharmonic response how close a system is to the edge of failure?* (2) *What is the effect of temperature? Could the anharmonic quasi-localized modes be responsible for phenomena associated with the glass state, such as the excess number of excitations, or dynamical heterogeneities that appear as the glass transition is approached? In particular, how is the jamming transition related to the glass transition?* (3) *How do generalizations of the model, such as non-spherical particle shapes, attractive interactions, and three-body interactions affect the picture developed for idealized spheres?*

FY 2012 HIGHLIGHTS

We analyzed the finite-size effects in jammed packings of soft, frictionless spheres at zero temperature and found that the contact number and elastic moduli exhibit scaling collapse with a nontrivial scaling function. This demonstrates that the jamming transition is a phase transition with an upper critical dimension of 2. We studied experimentally the dependence of the pair-correlation function, g(r), and particle mobility on packing fraction in a dense three-dimensional packing of colloids. As a function of packing fraction, there is a maximum in the height of the first peak of g(r). This peak is identified as the thermal remnant of the T=0 divergence found at the jamming transition in simulations. Our preliminary results show that we can continuously tune a system from perfect order to complete disorder. Many of the properties of the jammed solid are dominant and persist throughout nearly the entire range of order.

First-Principles Calculation of Vibrational Mode Lifetimes in Complex Materials

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PROGRAM SCOPE

We are implementing a practical method for calculating vibrational mode lifetimes in complex materials based on first-principles electronic structure calculations and for applying the method to several complex materials.

This proposal is aimed at a significant advancement in the calculation of lifetimes of vibrational modes. The approach is to implement a recently developed scheme for calculating mode lifetimes. (See Dickel & Daw, *Comp Mat Sci*, v47 p698 and v49 p445, 2010). The approach is based on techniques in non-equilibrium thermodynamics, using principally the Liouvillian operator to obtain dynamics, and is combined with the recursion method to study the properties of the resolvent. The result is an expression for the lifetime of a normal mode that is based on Monte Carlo evaluation of operators related to the mode occupation. This technique represents a substantial improvement over existing techniques.

The first milestone will be testing the method for some simple, low-dimensional models of anharmonic behavior. Second, we will extend the testing to three-dimensional lattice models of non-linear vibrations. Third, we will write extensions to the Sandia LAMMPS atomistic simulation package to carry out the calculations for semi-empirical potentials. Investigations at that stage will be conducted to investigate some systems that are treatable with semi-empirical potentials. Based on our experiences with semi-empirical potentials and LAMMPS, we will then plan the further extension to a first-principles electronic structure code.

FY 2012 HIGHLIGHTS

Funding for this program began near the end of the year. A qualified graduate student has been recruited, and we began work by writing codes to perform the calculations on simple, low-dimensional models. The results will be published in the project's first paper and will be helpful in guiding the later work.

Quantum Mechanical Simulations of Complex Nanostructures for Photovoltaic Applications

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PROGRAM SCOPE

This research project involves theoretical studies of complex semiconducting nanomaterials and their interfaces with other materials for next-generation photovoltaic cells. The central challenge in materials simulation is to address complexities in real materials, rather than only consider the properties of idealized materials or structures. In particular, for photovoltaic devices, electronic excitations due to optical perturbation are the principal properties; and it is of paramount importance to be able to accurately predict excited-state properties of complex nanostructures. However, current quantum mechanical simulation methods are either computationally too demanding or not accurate enough. The primary objectives of this project are: developing a new theoretical approach for electronic excitation calculations that are both accurate and applicable for large and complex systems, and applying the new methodology to investigate complex nanostructures that have great potential for opening new routes towards designing materials transport, electronic, and optical properties for photovoltaic and other optoelectronic usages.

RECOVERY ACT - New States of Matter and Quantum Simulation with Ultracold Alkaline Earth Fermions

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PROGRAM SCOPE

The goal of this project is to explore the potential of quantum many-body systems in novel regimes to realize new states of matter. Two classes of systems are being studied: (1) Some fermionic alkaline earth atoms have large nuclear spins, which enjoy a spin rotational symmetry highly enhanced above the three-dimensional rotational symmetry of space. This enhanced symmetry leads to novel many-body physics in ultracold alkaline earth atom systems, an area of increasing experimental activity. We have shown some such systems are cousins of solid state geometrically frustrated magnets, but with unique properties not present in any solid state materials, and that such systems are candidates to realize a variety of remarkable new states of matter. Particularly exciting is the prospect to realize a chiral spin liquid; if found experimentally, this would be the first state of matter with intrinsic topological order outside the fractional quantum Hall regime. We are exploring the possibility of realizing chiral spin liquids and other remarkable new states of matter in ultracold alkaline earth fermions. (2) In transition metal oxides with *5d* electrons (e.g., iridates, osmates, etc.), large spin-orbit coupling is combined with significant electron correlation, leading to a variety of interesting phenomena. We are particularly focused on systems where the strongly spin-orbit coupled *5d* electrons are coupled to local magnetic moments, arranged either in a regular lattice or as isolated magnetic impurities, and lattice defects (e.g., dopant atoms). Phenomena of interest include novel magnetically ordered topological phases induced by coupling to local magnetic moments, novel Kondo effects, and effects of dopants on the *5d* electronic structure.

FY 2012 HIGHLIGHTS

We have undertaken the first microscopic study of coupling between local rare-earth moments and *5d* conduction electrons in $R_2Ir_2O_7$ pyrochlore iridates, and shown that this coupling can help stabilize the recently proposed topological Weyl semimetal. This observation is likely to be particularly relevant for $Nd_2Ir_2O_7$. In the coming period, we plan a number of investigations on coupling of *5d* electrons with magnetic impurities and dopant atoms. We also envision collaborating with Jun Ye and Ana Maria Rey on near-term experiments to directly probe many-body effects of enhanced spin rotation symmetry in ultracold alkaline earth fermions.

CMCSN Many Body Methods from Chemistry to Physics and Back

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Funding:	$320,000

PROGRAM SCOPE

In this multi-investigator collaborative project, scientists including Garnet Chan (Chemistry, Princeton), Chris Marianetti (Materials Science, Columbia), Andrew Millis (Physics, Columbia; Project Director) and David Reichman (Chemistry, Columbia) aim to merge methods and insights recently developed in chemistry, materials science, and physics to create new approaches to the grand-challenge problem of calculating the properties of molecules and materials with strong electronic correlations. The theoretical challenge is to combine an accurate treatment of the fully entangled multielectron states characteristic of correlated electron phenomena with the material-specificity needed to make reliable statements about actual molecules and solids. Significant progress has been made in the separate disciplines of chemistry, materials science, and physics. The proposed Computational Materials and Chemical Sciences Network is taking the next step forward by linking the different fields, applying configuration interaction and self consistent embedding methods developed in quantum chemistry to the problems of condensed matter physics, and applying dynamical mean field and tensor product methods developed in physics to the problems of quantum chemistry.

FY 2012 HIGHLIGHTS

Among the recent successes of the program is the development of a new ``configuration-interaction'' method for solving the equations of dynamical mean field theory. Dynamical mean field theory is by now a widely applied approach to calculating the ground state and excitation properties of materials such as transition metal oxides and actinides where electron-electron interactions crucially affect the properties. While the method has had many successes in model systems, its applicability to real materials has been limited by our inability to solve the basic equations of the theory. The new methods developed in the CMCSN grant have the potential to greatly expand the range of applicability of the method.

The CMCSN group has also developed DMET, a new quantum embedding theory for predicting ground-state properties of bulk condensed matter systems. Like dynamical mean-field theory (DMFT), DMET maps the bulk interacting system to a simpler impurity model and is exact in the non-interacting and atomic limits. Unlike DMFT, DMET is formulated in terms of the frequency-independent local density matrix, rather than the local Green's function; and it features a finite, algebraically constructible bath which exactly embeds ground-states at a mean-field level with no bath discretization error. Frequency independence and the minimal bath make DMET a computationally simple and very efficient method. The method has been tested on model systems, and applications to actual materials are now being explored.

Theory of Surface and Interface Physics of Correlated Electron Systems

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Funding:	$150,000

PROGRAM SCOPE

Correlated electron materials have many striking and potentially important electronic properties including magnetism and superconductivity with very high transition temperatures, the ability to be switched from conducting to insulating behavior, and highly enhanced optical and magnetic responses. The materials can now be grown with atomic precision in ultra-thin film and atomic-scale heterostructure form. This research is aimed at developing the new theoretical methods needed to understand these new forms of matter and applying them to understand experiments and create new functionalities.

FY 2012 HIGHLIGHTS

We have solved a 30 year old problem by determining the mechanism underlying the metal-insulator transition of rare-earth nickel based perovskites. We have also provided fundamental new insight into the general theory of the correlation-driven metal-insulator transition emphasizing the role of hybridization in changing the valence of the transition metal site and have determined the theory of a class of ellipsometry experiments that are providing fundamental new insights into the physics of electrons at oxide interfaces

Bridging the Quantum-Chemistry Solid-State Divide: Theory and Application to Molecular Crystals

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PROGRAM SCOPE

Consider an excitation in an organic molecular crystal involved in solar energy conversion. First, a photon creates a local electron hole pair—a molecular event. This excitation may be broadened or shifted in frequency because of neighboring molecules—a solid-state effect. The exciton then rapidly diffuses to a local grain boundary—a feature of a crystal, or a large molecular cluster—where it feels a local impurity potential and dissociates back onto individual molecules.

This snapshot of the life of an exciton illustrates the key scientific challenges we face in the organic molecular crystal problem. To understand the electronic structure requires not only bridging many length scales in the problem, but also bridging the languages and techniques of chemistry (molecules) and physics (crystals). Our work establishes the tools to bridge these gaps. We focus on two main areas. The first is reducing the complexity of many-electron formulations using tensor factorizations. In this way, we lower the computational scaling of many-electron wavefunction methods used in Chemistry and Green's function techniques used in physics so that they can be applied not only to individual molecules but large aggregates. The second is joining local and extended electronic structure. Here we focus on embedding methods, using density functional, density matrix, and Green's function formalisms, to incorporate long-range electronic and polarization effects of the environment.

FY 2012 HIGHLIGHTS

We published several papers about tensor factorizations for local correlation methods. Our orbital-specific virtual (OSV) tensor networks now yield the fastest local correlation algorithms for "standard" quantum chemistry methods. OSV versions of Moller-Plesset second-order perturbation theory, and coupled cluster singles and doubles with perturbative triples (the "gold-standard" of quantum chemistry) theory are now widely available and distributed through the Molpro program package.

Using these tools, we can directly compute converged binding energies and properties of molecular crystals in a systematically improvable way. We have demonstrated this for the benzene molecular crystal. Our computed binding energy has a theoretical error bar significantly lower than the experimental error bars. Over the year, we will progress to more complex crystals including crystalline pentacene, as well as study properties such as charge and optical gaps.

Quantum Chemistry via Walks in Determinant Space

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Funding: $73,000

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 DOE. Another goal is to have cross-fertilization of ideas between i-FCIQMC and phaseless Auxilliary Field quantum Monte Carlo (AFQMC), developed by the Zhang-Krakauer group, since both methods employ walks in a space of determinants.

FY 2012 HIGHLIGHTS

In collaboration with M. Peter Nightingale at the University of Rhode Island, we have succeeded in making a very large improvement to the i-FCIQMC method. Quantum Monte Carlo methods are stochastic implementations of the power method for projecting onto the dominant state of a matrix or integral kernel. Recognizing this, the basic idea of our Semistochastic Quantum Monte Carlo (SQMC) method is to identify a small subspace of say 10 3 — 106 important determinants in which the projection is done deterministically. Only transitions for which both the initial and the final state are within the subspace are treated deterministically, the rest are treated stochastically. Since deterministic projection has no statistical error and no sign problem, this results in a large gain in efficiency.

We have also developed a procedure for using multideterminantal trial wave functions (the i-FCIQMC method uses just the Hartree-Fock determinant). The local energies required for calculating the mixed estimators are precomputed, and so there is no increase in the computational time during the Monte Carlo part of the run.

These two improvements have been implemented both for chemical systems and for the Hubbard model. We find that they result in 2-3 orders of magnitude gain in the computational efficiency. Not only is SQMC much more efficient than the i-FCIQMC, but in some cases, the initiator bias is significantly reduced.

We have also been collaborating with Garnet Chan at Princeton and Takeshi Yanai in Japan to explore using F12 methods to enhance convergence to the infinite basis limit.

Quantum Phases of Nanowires: Quantum Monte Carlo Approaches

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PROGRAM SCOPE

Electron-electron interactions cause a variety of quantum phase transitions (QPT) in nanoscale systems; the control and engineering possible experimentally in such systems then allows the QPT to be probed and manipulated in detail in both equilibrium and non-equilibrium contexts. Such QPT are thought to underlie many of the striking phenomena in contemporary exotic materials. The research in this program addresses such QPT in quantum wires and quantum dots as model systems.

In a quasi-one-dimensional wire, the positional order of the electrons can vary from extended liquid-like to localized Wigner-crystal-like. We use quantum Monte Carlo techniques to study the nature of the ground state wavefunctions. Within the localized regime, symmetry about the axis of the wire can be spontaneously broken; and we study the QPT from a linear arrangement to a zigzag phase.

Quantum dots connected to leads and reservoirs lead to QPT in a variety of situations. We study a quantum dot containing a resonant level connected to dissipative leads. The goal is to show how experiments in this system reveal the properties of exotic correlated states of matter.

FY 2012 HIGHLIGHTS

One key result this year was from our collaboration with the BES-funded experimental group of Gleb Finkelstein. We studied quantum mechanical tunneling of an electron through a resonant level (quantum dot) connected to resistive leads. Strikingly, there is a single point in parameter space at which the electron is fully transmitted while, at all other points, the conductance is zero. We explain this by showing that the dissipation in the leads generates an effective Luttinger-liquid-like interaction between the electrons. Our analysis reveals a splitting of the resonant level into two quasi-independent Majorana modes—one strongly hybridized to the leads and the other tightly bound to the quantum dot. Residual interactions involving these Majorana fermions result in the observation of a striking quasi-linear non-Fermi-liquid scattering rate at the QCP. Although unlikely to be practical for quantum computing, the device constitutes a viable alternative to topological superconductors as a platform for studying strong correlation effects within Majorana physics.

Correlated Electrons in Reduced Dimensions

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Funding:	$70,000

PROGRAM SCOPE

This project is focused on the properties and potential uses of topologically ordered states of matter. Topics of interest include so-called *non-Abelian* states, such as (we believe) the ν = 5/2 quantum Hall state, as well as possible phases associated with both regular and disordered arrays of interacting quasiparticles in these systems. In addition, the effects of the strong Chern-Simons gauge fluctuations associated with the composite fermion description of the bilayer ν = 1 quantum Hall state (valid for large layer spacing) on the possible instabilities of that state as the layer spacing is decreased are under investigation. Finally, work is being done in the rapidly developing area of surface codes. Here the essential idea is to use the remarkable properties of topologically ordered matter to carry out fault-tolerant quantum computation using more conventional qubits (e.g., superconducting qubits, trapped ions, electron spins in quantum dots, etc.). This is done by using these qubits to simulate a topologically ordered state which is then manipulated in such a way that a computation is carried out. This approach has been shown to have significantly less stringent requirements on qubit coherence and gate accuracy than previous fault-tolerant quantum computation schemes. In our work, particular emphasis is placed on proposing experiments that can feasibly be carried out using existing qubit systems and that begin to probe the requirements for carrying out quantum computation using surface codes based on non-Abelian topological order.

FY 2012 HIGHLIGHTS

We have completed a numerical study of chains of interacting non-Abelian quasiparticles using a novel generalization of the valence-bond Monte-Carlo method, which allowed us to introduce a new method for studying the crossover from weak to strong disorder in these systems [see H. Tran & NEB, PRB 86, 165113 (2011)]. In the area of surface codes, we were able to construct explicit quantum circuits using standard elements (single qubit rotations, CNOT gates, and Toffoli gates) for measuring the commuting set of vertex and plaquette operators that appear in the Levin-Wen model–a lattice model with non-Abelian topologically order [see NEB and D.P. DiVincenzo, PRB 86, 165311 (2012)]. Such measurements are required to detect errors in the surface code defined by the ground states of this model. We quantified the complexity of these circuits with gate counts using different universal gate sets and found these measurements become significantly easier to perform if n-qubit Toffoli gates (with n=3,4,5) can be carried out directly. In addition to our full measurement circuits, we constructed a number of closely related quantum circuits which require only a few qubits and which can feasibly be carried out experimentally using existing technology.

Strongly Correlated Electrons

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Funding:	$55,000

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, issues of the complex phase diagrams of transition metal oxides (manganites, ruthenates, and iridates), and the mesoscopic properties of quantum wires and quantum dots. 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 and/or electrical fields.

In particular, the present study addresses (1) the precritical fluctuations to the quantum critical point, giving rise to non-Fermi-liquid behavior for the Anderson lattice with a nested Fermi surface; (2) the interplay of ferromagnetism with other long-range order in UGe_2; (3) electron spin resonance in heavy fermion systems; (4) anomalies arising due to a Lifshitz transition; (5) the complexity of the rich phase diagrams in manganites, ruthenates, and iridates; and (6) mesoscopic systems, such as quantum dot spin valves and interacting quantum dots. Methods to be employed are renormalization groups, slave bosons, bosonization, the quantum inverse scattering method, and Bethe's ansatz, wherever applicable.

FY 2012 HIGHLIGHTS

(1) A discontinuous transition observed in the heavy fermion compound $CeIn_3$ in high magnetic fields was shown to arise from a Lifshitz transition due to the interplay of the Landau quantization and interactions. (2) A theoretical explanation was given for electron spin resonance (ESR) that can be observed in heavy fermion lattices with ferromagnetic correlations. Of particular interest is the case of the cubic compound CeB_6 which has a Γ_8 ground quadruplet with antiferro-quadrupolar long-range order. (3) The phase diagram of interacting ultracold atoms confined to a one-dimensional optical trap has been studied for arbitrary spin using the Bethe Ansatz and conformal field theory. The system displays phase separation along the trap and instabilities to superfluid phases with FFLO signatures.

Computational Approach to Complex Interfaces and Junction

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Funding: $180,000

PROGRAM SCOPE

The scope of this project spans fundamental physical processes at interfaces and across nano-molecular-junctions, with emphasis on electronic transport, via large-scale computation and simulation. Theoretical treatment for electronic degrees of freedom 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, van der Waals corrections, etc., are used to calculate physical and chemical quantities needed for addressing problems and issues. We focus on problems in complex interfaces and junctions, including (1) electron transport through metal-azobenzene-molecule-metal junctions, where the molecule can transform between trans and cis configurations in response to light excitation; (2) bonding, atom diffusion, and magnetization in systems containing the tris(8-hydroxyquinolino) aluminum (Alq_3) molecule between two magnetic leads, for its role as an insulator spacer in magnetic tunneling junctions; and (3) 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. One common theme unifying these systems is that interfacial structure has critical effects on properties, and our investigations based on first-principles can provide not only interpretation but also guidance for experiments on these seemingly vastly different systems. Finally, we include a major effort to develop a new method and algorithms. Based on scattering theory, our method combines a layer approach and a planewave basis in conjunction with pseudo-potentials. The method is optimal for studying electron transport across molecular- and nano-junctions.

Theory of Novel Superconductors

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Funding: $105,000

PROGRAM SCOPE

On the 100th anniversary of the discovery of superconductivity, the field is still vital and full of major challenges driven by the discovery of new materials, most of which appear to be very different from conventional superconductors. This project is devoted to understanding how novel superconductors work. The iron-based superconductors were discovered in 2008 and have captured the attention of the superconductivity community because, with the existence of a 2nd class of unconventional superconductors after the cuprates, one can now try to extract the essential ingredients for the occurrence of high temperature superconductivity. Similarities between these systems, heavy fermion superconductors, and organic superconductors are being explored. It is generally believed that the electrons in these materials form Cooper pairs, bound not by forces arising from ionic polarizations but by electron-electron forces themselves. A theory sometimes called “multiorbital spin fluctuation theory,” developed in part by the P.I., shows great promise in predicting the properties of the superconducting state. Because it is based on the electronic band structure calculated by first principles methods, there is the hope that one can develop a quantitative theory of unconventional superconductivity for the first time to guide the search for new superconductors. The project proposes several studies designed to identify the essential ingredients, both structural and electronic, of such a theory.

TMS: Orbital-Free Quantum Simulation Methods for Application to Warm Dense Matter

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Funding:	$0.00 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

This project is developing reliable finite-temperature, orbital-free density functional approximations for ab initio molecular dynamics simulations. Motivation comes from an urgent need to eliminate the Kohn-Sham bottleneck (computational costs scaling up as the cube of the number of occupied one-electron states) in quantum-forces-driven molecular dynamics. Evident at T = 0 K, the bottleneck grows in severity such that in the Warm Dense Matter (WDM) regime, it is a major limitation on realism (system size, MD run length). Additionally, we have provided evidence that WDM physics requires authentic free energy functionals rather than relying on ground state functionals as has been majority practice.

The WDM regime is of rapidly growing importance as an exotic form of condensed matter found along the path to inertial confinement fusion and in giant planet interiors. Characterized by electron temperatures ≈ 1-15 eV, pressures to 1 Mbar or higher, and densities from 10\% of ambient solid to 150-fold or more compression, there is no small parameter, hence no perturbative approach. Standard solid-state electronic structure methods are limited and standard plasma methods more so.

FY 2012 HIGHLIGHTS

(1) In the area of new functionals, we published an analytical framework of formulating generalized gradient approximations for the non-interacting free energy (kinetic energy and entropic functionals) and demonstrated substantial improvement over existing ad hoc functionals with our first approximation [Phys. Rev. B 86, 115101 (2012)]. We published a systematic comparison of existing finite-T vs. ground state exchange-correlation (XC) functionals vs. thermal Hartree Fock (see below), which shows the limitations of using ground state XC functionals [Phys. Rev. E. 86, 056704 (2012)]. We published several different variants on a general scheme to get new ground-state orbital-free X

functionals (to provide the proper low-T limit necessary to describe WDM atomic and molecular physics) [J. Chem Phys. 136, 104108 (2012); ibid. 136, 144115 (2012); Chem. Phys. Lett. 543, 179 (2012)].

(2) Regarding rigorous results, we provided a systematic development of the classical-map hypernetted chain scheme for getting quantum density functionals from classical statistical mechanics [Contrib. Plasma Phys. 52, 100 (2012)] and have a manuscript on finite-T scaling of interacting systems from dimensional analysis almost completed, as well as another on small-N modifications of Thomas-Fermi.

(3) In computational innovation, we published the first-ever implementation and use of the thermal Hartree-Fock (tHF) approximation in a confined system, including a new basis set, new code, and new results [Phys. Rev. B 85, 045125 (2012)]. We demonstrated that standard algorithms for solutions of the Kohn-Sham equation work poorly or not at all as solvers of the orbital-free DFT Euler equation. We also gave procedures for developing the local pseudopotentials required in orbital-free treatments with a plane wave basis [Comput. Phys. Commun. 183, 2519 (2012); Phys. Rev. E 86, 056704 (2012)].

K-Edge Resonant Inelastic X-Ray Scattering in Strongly Correlated Materials

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Funding:	$90,000

PROGRAM SCOPE

The emphases of this work are to develop new algorithms and solve and analyze the solutions for a range of different pump/probe types of experiments taking place in the ultrafast regime. Examples include time-resolved photoemission spectroscopy where experiments have recently examined charge density wave systems and seen a transient filling in of the gap with a nonvanishing order parameter. Another example is high harmonic generation in the solid state from applying a pump that generates Bloch oscillations, whose Fourier components are odd multiples of the fundamental frequency of the pump pulse. Our work will strive to understand and explain these experiments as well as examine newer experiments like time-resolved x-ray absorption spectroscopy or time-resolved Compton scattering. Our main emphasis is on exact solutions which can be found for noninteracting models, or with techniques like dynamical mean-field theory, generalized to nonequilibrium situations. We are part of a CMCSN team on pump/probe spectroscopies (also supported by DOE), collaborating with the Devereaux group at SLAC and Stanford as well as with international researchers in the Ukraine and India.

FY 2012 HIGHLIGHTS

We have completed papers on (1) RIXS in the Falicov-Kimball model described by dynamical mean-field theory; (2) XPS, XANES, and XAS in the same model; (3) thermalization of a Mott insulator after hitting it with an intense pump pulse; (4) high order harmonic generation via Bloch oscillations in solids; and (5) pump/probe Compton scattering for electron-phonon interacting systems. We also are writing about work on pump/probe time-resolved photoemission spectroscopy in charge density wave systems.

First-Principles Investigation of Complex Materials Properties

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Funding:	$155,000

PROGRAM SCOPE

This project concentrates on studying complex materials properties using first-principles electronic-structure methods. 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 and semiconductor nanowires. Graphene has been recognized as a unique system containing two-dimensional fermions with linear dispersions near the Fermi level. The recent success in fabricating graphitic samples consisting of only a few layers of carbon sheets has revealed intriguing properties of this system. We have initiated a computational effort to investigate the special electronic properties of twisted bilayer graphene and demonstrate that combining two graphene layers enables us to probe the rich physics involving multiple interacting Dirac fermions.

FY 2012 HIGHLIGHTS

The Hofstadter butterfly spectrum for Landau levels in a two-dimensional periodic lattice is a rare example exhibiting fractal properties in a truly quantum system. It turns out that, for a specific range of rotational angles, twisted bilayer graphene serves as a special system with a fractal energy spectrum under laboratory accessible magnetic field strengths. This unique feature arises from an intriguing electronic structure induced by the interlayer coupling. In this study, we systematically map out the spectra of these Landau levels (LLs) as a function of the rotational angle. Our results give a complete description of LLs in twisted bilayer graphene for both commensurate and incommensurate rotational angles and provide quantitative predictions of magnetic field strengths for observing the fractal spectra in these graphene systems.

In addition, another important particle-physics phenomenon—a neutrino-like oscillation—can be studied and observed in twisted bilayer graphene. The quasiparticle states in two distinct graphene layers act as neutrinos with two flavors; and the interlayer interaction between them induces an appreciable coupling between these two “flavors” of massless fermions, leading to neutrino-like oscillations. Moreover, anisotropic transport properties manifest in this specific energy window, which is accessible in experiment for twisted bilayer graphene. By varying the twist angle and the initial wave packet, we can effectively control the propagation of electrons in twisted bilayer graphene.

Structure and Dynamics of Material Surfaces, Interphase-Interfaces and Finite Aggregates

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Funding:	$225,000

PROGRAM SCOPE

Investigations of fundamental materials physical and chemical processes and of the microscopic origins of materials properties, and explorations aiming at novel materials preparation and design, are major thrusts of modern materials science. This research program focuses on the development and implementation of computational and simulation methodologies of predictive capabilities, and their use as tools of discovery in a broad range of materials problems of fundamental and technological interest, pertaining to nanoscale systems. Topics of the proposed research and educational program include:

(1) Properties and Transport in Inorganic and Organic Nano-Structures – Wires and DNA.

(2) Confined Electron and Boson Systems: Quantum Dots, Atom Traps, Graphene Dots. Correlated electronic states in quantum dots under field-free conditions and in the presence of variable magnetic fields, formation of rotating electron molecules, prediction and interpretation of transport measurements on few-electron quantum dots as quibits in quantum computers, formation of crystallites in cold atom trap, formulation and construction of a universal quantal molecular description of the spectra of bosons and fermions in the lowest Landau level.

(3) Nanoclusters: charged water nano-droplets and artificial photosynthesis. (a) First-principles investigations of the size-dependent evolution of the states of water clusters (in the range of 15 to 200 molecules) with single and, in particular, double excess electrons. (b) Explorations of the compositional, geometrical, electronic, and reactivity characteristics of small metal clusters.

FY 2012 HIGHLIGHTS

(1) Joint First-principles theoretical and experimental investigations of atomic-scale mechanisms of mutations in DNA, involving proton-coupled electron transfer reactions of ionized DNA with water. The targets of our research are reactions of one-electron ionized A/T-rich regions in DNA and fundamental understanding of the sequence dependence and pathways of reactions underlying mutations, caused by endogenous and exogenous one-electron oxidation of A/T rich DNA, which are implicated in early stages of cancer development.

(2) Investigations of metal/water cluster complexes, and first-principles explorations of the elementary steps of charging and water splitting reactions. These first-principles simulations, jointly with laboratory experiments, aim at contributing to the development artificial photosynthesis systems.

(3) Computational explorations of the properties of confined electron systems which exhibit highly correlated electron states and spontaneous symmetry breaking, weak disorder in two-dimensional electron gases underlying Wigner crystallization under fractional quantum Hall effect conditions, semiconducting, metal, and graphene quantum dots (QDs) at field-free conditions and under the influence of magnetic fields, Aharonov-Bohm oscillations in graphene, edge reconstruction and edge

states engineering of the properties of graphene QDs, and optical properties of small graphene QDs targeted for possible application in photo-voltaics.

Theory of Electron Imaging in Small Devices

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PROGRAM SCOPE

The transport of charges in electronic devices is of substantial interest in fundamental and applied research. There is an important trend toward imaging electronic systems in real space, with the goal of understanding the specifics of individual samples rather than settling for ensemble and statistical descriptions. The imaging is often semi-direct and requires theory and interpretation to extract all that can be deduced about the underlying physical quantities. This is the case with scanning probe microscope imaging of systems in which the motion of the carriers is restricted to two degrees of freedom, such as in graphene and the two dimensional electron (and hole) gas (2DEGs and 2DHGs) in GaAs/AlGaAs heterostructures, or when the motion is restricted to one degree of freedom as in nanowires. This technology allows the tip of a movable charged probe to alter the electron gas locally, by depleting or alternatively increasing the amount of charges in the electron gas just below the tip, which can result in mirror-like or lens-like behavior of the affected region. This tunable region in turn affects, perhaps indirectly, the measured quantities such as conductance or transconductance.

An existing series of investigations, conducted by the Heller group in collaboration with the Westervelt group at Harvard, provides a library of documented collaborative discoveries where neither theory nor experiment was clear without the support of the other. In the funded research, we extend our understanding of coherent electron transport in the light of scanning probe imaging, in anticipation of new experiments and to further mine existing experiments for the information they contain. We undertake a detailed series of investigations that will enhance the imaging functionality and understanding of the transport properties at the nanometer scale and nanostructured materials. We address these challenges with state-of-the-art theoretical and computational tools to maximize understanding of the experiments.

FY 2012 HIGHLIGHTS

This past year we have made significant progress in the research program funded by the department of energy and have several accomplishments to report:

(1) Regarding cold collisions of complex polyatomic molecules, we worked with postdoctoral fellow Zhiying Li and introduced a method for classical trajectory calculations to simulate collisions between atoms and large rigid asymmetric-top molecules.

(2) Regarding the development of a semiclassical interpretation of probability flux, we worked with graduate student Douglas Mason and research associate Mario Borunda and have developed a new

interpretation of the probability flux operator by deriving its eigen- states and relating them to coherent state projections on a quantum wavefunction.

(3) The theory of scanning probe imaging of graphene nanostructures extends our previous theory-experiment collaboration that studied scanning probe imaging in graphene systems.

(4) Regarding optical quantum control of entangled states in quantum wells, we worked with visiting scientists Esa Rasanen (researcher at University of Jyvaskyla, Finland) and Thomas Blasi (Diplom student from Technische Universitat Munich, Germany) and research associate Mario Borunda and developed theory and performed calculations towards coherent high-fidelity quantum control of many-particle states in semiconductor quantum wells.

(5) Regarding coherent quantum electronics by means of spectral navigation, we worked with research associate Mario Borunda, visiting scientists Esa Rasanen and Thomas Blasi, and professor Robert Westervelt and described a scheme for the coherent manipulation of the electronic degree of freedom in a semiconductor double-quantum dot system containing two electrons.

Non-Equilibrium Physics at the Nanoscale

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Funding: $70,000

PROGRAM SCOPE

This program focuses on (1) understanding the microscopic origin and the relevant physical quantities that determine non-equilibrium transport (both charge and excitonic) in nanoscopic quantum networks, (2) exploring the emergence of strong correlations at the nanoscale, and (3) combining the results of these projects to design nanoscale quantum structures with new functionalities that utilize the balance between quantum coherence and noise. Of particular interest for this program are systems where (1) correlation effects arise from strong interactions; (2) a complex bandstructure allows for the emergence of novel quantum phenomena, as is the case in grapheme; and (3) topologically non-trivial bandstructures are induced by interactions, such as in topological insulators. The question of how non-equilibrium transport occurs in these systems at the nanoscopic level is not only of fundamental interest for our understanding of quantum phenomena at the nano-, meso and macroscale, but also of great importance for the further development of nano- and molecular electronics as well as for the continued miniaturization of electronic devices and the fabrication of artificial quantum structures.

FY 2012 HIGHLIGHTS

We have proposed a novel method using a scanning tunneling microscope that allows for the first time to image spatial current patterns in nanoscopic quantum networks with atomic resolution. We demonstrated that this imaging technique can be successfully applied in a variety of network topologies and lattice structures, with mean free paths ranging from infinity (ballistic limit) down to a few lattice constants. Moreover, we showed how the unique electronic structure of nanoscopic graphene lattices gives rise to complex spatial current patterns and demonstrated how these patterns evolve with increasing dephasing. We extended our work to study energy transport (in the form of excitonic currents) in biological complexes and demonstrated how the coupling to external phonons alters the current paths in the complex and increases its efficiency and conductivity.

SciDAC Partnership: Predictive Computing for Condensed Matter

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Students: 1 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding: $690,000

PROGRAM SCOPE

Fundamental progress in energy technology depends critically on our ability to fabricate, characterize, and optimize advanced materials that can convert, transport, and store energies. To achieve this, we must be able to understand materials' properties from first principles and to design new materials with predicted useful properties. We must also harness the non-abating increase in computing power such as at DOE's leadership supercomputers. It has been clear, however, that today's standard computational method for solids, i.e., density-functional theory (DFT), is fundamentally limited in its ability to predict response or excited-state properties as well as any properties of strongly correlated solids. Efficient, robust, parallel software implementing new *ab initio* methods that go beyond DFT are needed for materials and chemical processes in condensed phases, enabling chemists and physicists to predict virtually any observable at arbitrary high accuracy. Our proposed research consists of three components:

(1) Theory: We will establish novel electronic structure theories for solids that are predictive in the sense that the fidelity of simulation can be increased systematically, and hence the calculated results are guaranteed to converge at the exact solutions of the Schrödinger equation; that can handle excited electronic states and thus response properties, going beyond the usual one-electron picture; and that can be applied to strongly correlated electronic structures by exposing hidden mathematical structures and symmetries therein.

(2) Software: We will create a suite of software implementing the predictive electronic structure theories for solids, which are, by virtue of exploiting novel software technologies and new algorithms, to be simultaneously scalable, extensible, and maintainable despite complex, diverse, and rapidly evolving supercomputer architectures.

(3) Applications: We will apply these predictive methods as implemented in highly scalable parallel software to some of the outstanding condensed matter problems, including unexplained experimental results for high-temperature superconductors and the excited states in graphene.

FY 2012 HIGHLIGHTS

The project was launched in September 2012, involving six groups of chemists and physicists across three institutions (University of Illinois at Urbana-Champaign, Princeton University, and College of Williams and Mary). We have begun hiring able graduate students and postdoctoral researchers and conducting joint weekly meetings in Urbana, also attended by external participants through Skype. A collaborative application subproject on cuprate superconductors and collaborative development subprojects on a strong correlation method and stochastic perturbation theory are being started.

The funding shown is for all institutions.

Laser-Induced Ultrafast Magnetization in Ferromagnets

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Funding:	$110,000

PROGRAM SCOPE

This program focuses on the emerging field of laser-induced femtosecond (fs) magnetization in ferromagnets or femtomagnetism with potential applications in magnetic recording. Our goal is to reveal the mechanism of ultrafast demagnetization and to train young researchers and students through active research and education. To achieve this goal, we use nickel as an example. We first compute the laser-induced spin and orbital momentum changes and establish the missing link between spin and orbital dynamics. Then we develop a new algorithm for two ultrafast x-ray based and element-specific techniques. This enables us to directly compare our theoretical results with experimental ones. Two immediate impacts from the proposed research are (1) it will reveal how the orbital degree of freedom and light polarization affect the magnetization change and (2) it will establish a new speed limit for the future magnetic recording.

FY 2012 HIGHLIGHTS

Up to now, we have discovered a new method to characterize the spin change in the crystal momentum space. This method is called Spin-Dipole factor method, which is very useful. In addition, we have developed a new program that can include the electron correlation effect in the entire demagnetization process, which has not been done previously. In the meantime, we started on a much more complicated system to see whether it is possible to change the magnetic properties via laser and strain. These results have been published.

Theory of Fluctuations in Superconductors

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Funding:	$103,000

PROGRAM SCOPE

This project focuses on the theoretical studies of fluctuation phenomena in superconductors. The physical systems of interest include two-dimensional disordered superconducting films, high-temperature cuprate superconductors, superconducting proximity systems, superconducting heterostructures involving nanowires and ferromagnets, and topological superconductors. The main goals of the proposed research are to improve fundamental understanding of these systems and to provide solid theoretical basis for a number of relevant recent and ongoing experimental studies. Another ambitious component of this proposal is to develop a substantially new theoretical framework to investigate non-perturbative quantum fluctuation effects in broken-symmetry phases of quantum matter.

FY 2012 HIGHLIGHTS

In a recent paper [Phys. Rev. B 86, 054521 (2012)], we developed a comprehensive theory to describe an experiment of the PennState group [Wang et al., Nature Physics 6, 389 (2010)], which observed an anomalously long-ranged proximity effect from a normal superconductor into a ferromagnetic Cobalt nanowire. It was proposed that the origin of the effect is due to spin-orbit-coupling at the interface, which enables the single Cooper pairs to be converted into triplet Cooper pairs in the nanowire. It was also suggested that this type of a setup will be ideal for creating Majorana fermion excitations. Motivated by these ideas, we are guiding an experimental effort to create a topological superconductor in diluted magnetic semiconductor/superconductor structures.

In a related paper [http://arxiv.org/abs/1206.3226, to be published in Phys. Rev. B], a theory of Majorana fermions in high-temperature-superconductor/ferromagnet junctions have been developed.

In another paper [http://arxiv.org/abs/1209.1105], the PI and his postdocs have proposed and developed a theory of an experiment that should enable us to determine whether there are paired electron pockets in the pseudogap phase of the high-temperature cuprate superconductors. The idea of the experiment is to perform ARPES measurements in the presence of a transport current running through the sample, that is predicted to open up the ghost electron pocket.

Strongly Correlated Electronic Systems: Local Moments and Conduction Electrons

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Funding:	$160,000

PROGRAM SCOPE

A Majorana fermion is a fermion which is its own antiparticle. It is sometimes described as half a fermion because a conventional creation operator can be written as $f^\dagger = a + ib$, where a and b are Majorana operators satisfying $a = \mathrm{a}^\dagger$, $b = b^\dagger$. If a Majorana fermion is localized in space, it is expected to obey non-Abelian statistics, i.e., the exchange of two such localized objects lead to a new state vector in the Hilbert space, as opposed to a sign change or a change in the phase of the wavefunction in the case of fermions or anions. These objects have attracted great interest because they have been proposed as the first step towards fault tolerant topological quantum computers. Regardless of potential applications, it is clear that these objects are of fundamental interest in their own right, but up to now they have not been seen in Nature.

In solid state physics we are familiar with Bogoliubov quasiparticles in superconductors which are superpositions of particles and holes with amplitude u and v, respectively. If $|u| = |v|$ and if the quasiparticles are localized, they will form Majorana bound states (MBS) and will possess all the exotic properties described above. Under suitable circumstances, the MBS arises as a *single* zero energy mode in the solution of the Bogoliubov-deGennes (BdG) equation. For example, in a spin aligned $p_x + ip_y$ paired superconductor, a single MBS is predicted to exist as a zero mode in the vortex core. Unfortunately, $p_x + ip_y$ superconductors are not common in Nature. The goal of this project is to study practical schemes to produce MBS in the laboratory and to verify their existence.

FY 2012 HIGHLIGHTS

In early 2012 the Delft group announced the observation of signatures of Majorana bound states in semiconductor nanowires proximity coupled to a superconductor. The signature consisted of zero bias peaks which appeared under the application of a parallel magnetic field. This generated a great deal of excitement in the community. We are concerned about the effect of disorder, particularly disorder at the interface between the nanowire and the superconductor, which we previously showed to have a detrimental effect on the existence of the Majorana bound states. We carried out detailed simulations with parameters appropriate to the experiments, and we found that zero bias peaks similar to those reported may arise due to bound states formed by disorder near the ends of the wires. These are not topological in origin and are not true Majorana bound states. We concluded that more experimental data are needed and sample quality needs to be improved before claims of seeing a Majorana bound state can be accepted.

Unconventional Metals in Strongly Correlated Systems

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Funding: $115,000

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, it 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. In another project, he will study the evolution of transport quantities across a quantum phase transition associated with the death of a Fermi surface in Kondo lattice systems, and explore its relationship with the electron spectral function.

FY 2012 HIGHLIGHTS

Funding for this project began recently in mid-August 2012. Research supported by this funding is in progress as mentioned above.

Modeling the Self-Assembly of Ordered Nanoporous Materials

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Funding: $185,000

PROGRAM SCOPE

This research program is about modeling the synthesis of ordered nanoporous materials. These materials are of enormous importance in modern technology with traditional applications in catalysis and separations for the chemical process industries and more recent applications in areas like biosensing and microelectronics. The materials science and engineering of these materials focus on the development of materials that are tailored for specific applications through control of pore structure, size and shape as well as the chemistry of the material components. Through detailed modeling of the nanoscale assembly processes of these materials, we seek to provide a greater understanding that can be used in improved control of the synthesis outcomes as well as guidance in the discovery of new materials. Our focus is on two types of materials that both feature the formation of three-dimensional networks of polymerized silica. These are all-silica zeolite frameworks and ordered mesoporous silicas. In the first of these, the network structure is crystalline with nanoscale order created by small structure-directing agents or templates. In the second, the network structure is amorphous at the atomic length scale but ordered on the length scales in the range 2-10 nm through structure direction by larger surfactant molecules, block copolymers, or both. These represent two of the most important routes for the controlled synthesis of ordered nanoporous materials. Our research program has two main elements: (1) modeling polymerization processes in 3-d network solids including zeolite frameworks and (2) modeling ordered mesoporous materials synthesis by surfactants and block copolymers. Our research is based on the hypothesis that both of these kinds of systems can be understood in terms of a framework that focuses on modeling silica polymerization through the assembly of corner-sharing SiO_4 tetrahedral units. We have developed both lattice-based and off-lattice models for the assembly of corner-sharing tetrahedral.

FY 2012 HIGHLIGHTS

We have combined our atomic tetrahedral lattice model of silica together with the surfactant lattice model of Larson, to make a model of the surfactant templating of ordered mesoporous silica materials, e.g., MCM-41. When experimentalists fabricate MCM-41, they generally find that the best approach involves a two-step synthesis where the first step involves low temperature and high pH, while the second step requires higher temperature and lower pH. Our simulations are revealing insights into the mechanism of this two-stage process.

Charge Frustration, Spin Singlets and Superconductivity in the 1/4-filled Band Paired-Electron Crystal

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Funding:	$150,000

PROGRAM SCOPE

Correlated-electron superconductivity has remained a formidable theoretical problem in condensed matter physics after two decades of intensive research. While the greatest focus has largely been on the family of high T_c copper oxide superconductors and more recently on the pnictides, there exist many other materials that exhibit the same peculiar normal state behavior associated with repulsive interactions between the electrons. One characteristic that is shared by these materials is that superconductivity is nearly always proximate to an insulating state with spatial broken symmetry. A second characteristic is that, in many cases, the superconductivity is limited to a narrow range of charge-carrier concentration.

In the present theoretical research program, we are investigating the low temperature metal-insulator, insulator-insulator and superconducting transitions in seemingly unrelated families of materials, quasi-two-dimensional (2D) organic superconductors, 2D layered cobaltates, and three-dimensional inorganic spinels. Our goal is to provide a new starting point to understand unconventional superconductivity in these materials. We argue that the physics of these seemingly unrelated families of materials is dictated by the combined effects of electron-electron repulsion, the particular bandfilling of ¼, and charge frustration. We propose that the insulating state proximate to superconductivity in these materials is a Paired Electron Crystal (PEC), a charge-ordered state with spin-singlet dimers separated by pairs of vacancies. Within our theory, superconductivity results from pressure-induced enhancement of charge frustration on the PEC. In the present project, we investigate the ground-state properties and thermodynamics of the PEC state, as well as its connection to superconductivity, using a range of numerical many-body methods applied to model Hamiltonians.

FY 2012 HIGHLIGHTS

We completed large-lattice studies of the 1/2-filled 2D anisotropic triangular lattice Hubbard model commonly used to describe the electronic properties of organic superconductors. Within our correlated-electron calculations using the Path Integral Renormalization Group (PIRG) method, we find no superconductivity within this model. This reinforces our proposal that a 1/4-filled model is needed. We further began using exact diagonalization and PIRG to study the full 1/4-filled electronic model for these materials.

Charge and Spin Dynamics in Bulk and Heterostructured Dilute Magnetic Semiconductors

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Funding:	$105,000

PROGRAM SCOPE

This project is concerned with the dynamics of collective excitations of the itinerant carriers in dilute magnetic semiconductor (DMS). Ferromagnetic DMS have attracted much attention as a promising basis for spintronics devices. Intense research efforts across a wide community are dedicated to the transport and optical properties of DMS, such as (Ga,Mn)As. Our investigations will be in the following three areas: (1) 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) 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) 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, and electronic many-body effects.

FY 2012 HIGHLIGHTS

We teamed up with an experimental group at the University of Paris VI, where inelastic light-scattering experiments on asymmetric GaAs quantum wells were performed. The experiments confirmed an effect that was predicted by us 10 years ago: the dispersions of intersubband spin plasmons show a three-fold splitting due to the presence of spin-orbit coupling. The spin plasmon behaves as a macroscopic quantum object that precesses in an effective many-body spin-orbit field. This is contrary to expectations, whereby D'yakonov-Perel' dephasing should broaden the plasmon. We have also developed a new nonlocal formalism of calculating the spin plasmon linewidth caused by the spin Coulomb drag, which agrees well with experimental data. In the next year, we will extend these studies to other types of systems, such as spin waves in (Cd,Mn)Te quantum wells. The general theme is to study the interplay between electronic many-body effects and spin-orbit coupling in low-dimensional semiconductors.

Fundamental Studies of Complex Oxides and Their Interfaces

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Funding:	$130,000

PROGRAM SCOPE

The goal of this project is to develop a theoretical description of the physics of the correlated oxides and their interfaces, starting from the density-functional studies of the electronic structure. Correlated oxides include materials such as the colossal magnetoresistive manganites, high-T_c cuprates, Luttinger liquid lithium oxide bronzes, magnetite with its peculiar Verwey metal-insulator transition, and the new spin-ice and quantum-spin-liquid oxides. These materials come with complex crystal structures, with electron-lattice coupling via the Jahn-Teller interaction, competing magnetic interactions such as double exchange and super exchange, and the coupling between charge, spin, and orbital degrees of freedom. The recent growth of high-quality interfaces between correlated oxides such as $LaAlO_3$/$SrTiO_3$ has led to the discovery of novel phases of matter at the interfaces, with new fundamental science and prospects for bold new paradigms for future device applications. This project has a broad objective of understanding the many fascinating but ill-understood phernomena observed at the interfaces as well as in the bulk.

FY 2012 HIGHLIGHTS

There are three main projects under way.

(1) Rashba spin-orbit interaction at the oxide interfaces: We are studying how the Rashba spin-orbit interaction at the polar oxide surfaces can be tuned by an applied electric field and strain. These results are derived by studying the two-dimensional electron gas (2DEG) at the polar $KTaO_3$ surface using

density-functional methods. While the ``polar catastrophe" ideas, familiar from the perovskite interfaces, lead to the formation of the 2DEG at the polar surface including the distinctive subband structure, strong lattice relaxation at the surface reorients the subbands in such a way that the Rashba spin-orbit splitting in the band structure is weak, despite the presence of heavy elements. We find that an applied electric field or strain can substantially reorient the subband structure and produce a large Rashba spin-orbit interaction, leading to the possibility of novel applications in future devices.

(2) Quantum spin liquid in frustrated magnets: The geometrically frustrated material $Ba_3CuSb_2O_9$ has been recently proposed as a candidate for the quantum spin liquid state. We are studying the electronic structure and the Jahn-Teller effect in this material in order to understand the coupling between the Cu spins, responsible for the spin-liquid state.

(3) Skyrmion in MnSi: Another example of exotic spin state occurs in materials such as MnSi, where skyrmion spin ordering under an applied magnetic field has been recently observed. The fundamental ingredient for the formation of the skyrmion state is the Dzyaloshinskii-Moriya interaction, which plays a key role in stabilizing the skyrmion structure. We are studying the origin of this interaction in the B2 phase of MnSi, which arises from the anisotropic part of the super-exchange in a non-centrosymmetric structure.

Time-Dependent Current Density-Functional Theory of Charge, Energy and Spin Transport in Nanoscale Systems

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Funding:	$105,000

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 proposal, we continue our work towards a complete formulation of the transport problem using Time-Dependent Current Density-Functional Theory (TD-CDFT), and its recent extension to open quantum systems—(Stochastic) TD-CDFT. The main goal is to understand the dynamics of charge, spin, and energy in nanostructures from a microscopic point of view. Stochastic TD-CDFT is the natural framework in which this complex problem can be approached while keeping the solution to a computationally accessible level. Indeed, this formulation offers several advantages since it directly yields the current that flows in a conductor in response to an arbitrary time-dependent perturbation, including quite naturally inelastic electron-electron effects, as well as interactions with external environments.

The present project will accomplish the following goals: (1) development of the quantum continuum mechanics approach to the dynamics of nanoscale systems; (2) development of new exchange-correlation energy functionals for charge, spin, and energy dynamics; (3) introduction of a practical scheme for electrical current calculations for biased nanoscale systems using Stochastic TD-CDFT and its test on specific systems and phenomena; and (4) entanglement dynamics in nanoscale systems using (Stochastic) TD-CDFT. All of these projects are the first of their kind, and may have a large impact on the field of electronic transport and non-equilibrium statistical mechanics by introducing new ways of thinking about these problems and to calculate their solutions.

CMSN: Computational Design of Fe-Based Superconductors

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Funding:	$170,000

PROGRAM SCOPE

This CMSN collaboration comprises four nodes: Rutgers (G. Kotliar, K. Haule); University of Arizona (M. Van Shilfgaarde); University of California - Davis (S. Savrasov, W. Pickett); and Ames National Labs-Iowa State University (J. Schmalian, K.M. Ho, V. Antropov).

The goal of this CMSN is to develop a unified methodology for electronic structure calculations to estimate from first principles the physical properties of strongly correlated electron materials. The archetypical iron pnictides served as the arena in which to test of the methodologies and the codes. The goal of this CMNS was to integrate three different diverse methodologies, identify strengths and weaknesses, and optimize their combination to tackle one of the daunting challenges of electronic structure: how to treat from first principles the electron-electron interactions. Different aspects of the correlations can be treated by DMFT GW and Gutzwiller methods.

The conceptual integration of the LDA+Gutzwiller and the LDA+DMFT method was achieved by demonstrating formally that the former can be cast in terms of an accurate and fast DMFT impurity solver. In terms of code development, we have developed within the IOWA Rutgers collaboration a full potential LAPW Gutzwiller +LDA which allows a detailed comparison with the LDA+ DMFT code developed by K. Haule at Rutgers. A beta version of a Gutzwiller +LDA code in an LAPW basis set is available and has been used on iron pnictides and manganese pnictide superconductors. This code removes the shortcomings of the previous Guztwiller +LDA codes which introduced uncontrolled approximations due to the downfolding. Calculation of total energies are in progress.

FY 2012 HIGHLIGHTS

In a collaboration between Mark VanSchilfgaarde and the Rutgers node, the first quasiparticle GW calculation of the iron pnictide superconductors was carried out. The spectral properties appear to be significantly better than LDA (e.g., reduced bandwidth, improved Fermi surfaces). The frequency dependent correlations are very local, suggesting that QP GW +DMFT is the proper method for describing these materials. All of the chemical trends in the mass renormalizations in these materials are reproduced by the GW calculation, but quantitative agreement requires the use of DMFT. A paper reporting these results has been accepted for publication in *Physical Review Letters*.

Correlation Effects and Magnetism in Actinide: Elements and Compounds

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

PROGRAM SCOPE

Actinide based materials are of fundamental importance from a basic science perspective as model systems where we can explore the physics of strong correlations in elements and simple compounds. Understanding the solid state physics of actinides is also very important for DOE in view of their applications as nuclear fuels and to ensure the safe storage of already accumulated radioactive material.

The objective of our research program is to achieve a fundamental understanding of the solid state phases of materials containing elements from the actinide series. To reach this goal, we develop first principles relativistic electronic structure many body methods based on extensions of the Dynamical Mean Field Theory (DMFT) and apply them to elemental actinides and compounds. We then develop simplified models to guide the search for materials with desirable properties. We also develop DMFT based theoretical spectroscopies and use them to interpret the outcome of photoemission, optical conductivity, and neutron scattering experiments. With Andrey Kutepov, we applied self-consistent GW to elemental actinides.

FY 2012 HIGHLIGHTS

We have recently investigated the localization-delocalization crossover in delta Plutonium and in Pu 115’s, and we will present an overview of our current understanding of these materials thru the lens of DMFT based theoretical spectroscopies.

Spin and Orbital Physics in Novel Correlated Materials

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Funding:	$300,000

PROGRAM SCOPE

This proposal describes research on the role of coupled orbital, spin, and geometrically frustrated degrees of freedom as drivers of new kinds of correlated electron behavior. Three projects, involving the topological insulating behavior of heavy electron materials, the role of tetrahedral-based physics in the iron-based superconductors, and the emergent Berezinskii-Kosterlitz-Thouless physics of frustrated Heisenberg magnets, are described. The science behind these phenomena has an important role to play in establishing new concepts to underpin design and discovery of materials to transform our future.

Three topics grouped around the theme of spin and orbital physics are being pursued:

(1) Topological Kondo Insulators. We will investigate, in collaboration with experimental and computational physicists, the proposal that strongly spin-orbit coupled 4f states drive topological behavior in the family of Kondo insulators. We will develop a theory of cubic Kondo insulators, built around an analytical model, later extended with band-theory input. This model will be used to identify strong candidate topological Kondo insulators and to study the tunneling into the hybridized surface Dirac cones of a topological heavy electron insulator.

(2) A tetrahedral approach to the Iron-Based Superconductors. Research which will focus on the role of tetrahedral symmetry in the iron-based superconductors. Motivated by the correlation of superconductivity with tetrahedral symmetry, we will examine the effect of orbital Kondo fluctuations on the superconducting and nematic physics of these materials. We will employ analytic methods which take account of the staggered tetrahedral structure to examine a new class of staggered s+/− pairing with d-wave symmetry at the iron sites.

(3) Frustrated Magnetism and the Emergent Clock Model. Motivated by a renewed interest in the emergent discrete physics of frustrated Heisenberg antiferromagnets, we will study a family of Heisenberg models that develop an emergent n-fold order parameter de-scribed by the n-state Clock-model. Simple arguments suggest the possibility of an emergent Berezinskii-Kosterlitz-Thouless transition, which will be evaluated and explored in detail. This work will use analytic renormalization group methods, later supported by computational Monte Carlo work.

Tailoring Magnetism and Spin in Quantum Dots

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Funding:	$140,000

PROGRAM SCOPE

Magnetic doping of semiconductor nanostructures such as quantum dots (QDs) provides an interesting interplay of interaction effects in confined geometries and novel opportunities to control the ordering of carrier spin and magnetic impurities at the nanoscale. However, owing to the computational complexity of including even a small number (~10) of magnetic impurities, there is a greater need to apply various approximations schemes to describe magnetic QDs. Unfortunately, a widely used mean-field approximation neglects the thermodynamic spin fluctuations and shows serious problems, including spurious phase transitions, when applied to such small magnetic systems. These difficulties impede the progress in understanding of the fundamental properties and the potential applications of magnetic QDs. To systematically address this situation, our main objectives are to (1) develop a comprehensive framework suitable to study the interplay of many-body effects and quantum confinement in small magnetic systems and (2) explore novel possibilities to control the ordering of magnetic impurities and carrier spin in QDs, as well as to provide proposals for their experimental implementation.

FY 2012 HIGHLIGHTS

We have revealed several peculiar effects for magnetic ordering in QDs. For certain hole densities, we predict a reentrant temperature dependence of the magnetization; it disappears for some temperature ranges and reappears at higher temperatures. Our results show that such a reentrant scenario is indeed possible, not just in the mean-field approximation, but also with the fluctuation approach, when the statistical spin fluctuations are correctly taken into account. Some hints for such an unusual behavior could be already inferred from our prior experimental collaboration showing that magnetic polaron binding energy may increase with temperature. We have predicted spin-Wigner molecules, novel strongly-correlated phases in magnetic quantum dots which are nanoscale analog of Wigner crystallization. We show how magnetic impurities could provide novel ways to imprint correlation effects. We have explored different manifestations of magnetic anisotropy in QDs, extensively studied in bulk dilute magnetic semiconductors, but largely overlooked in magnetic QDs where it could play an important role, in transport phenomena, formation of magnetic polarons, control of magnetic ordering, non-volatile memory, and quantum bits. We have shown that tuning the quantum confinement allows a control of magnetic easy axis in QDs in ways not available in bulk dilute magnetic semiconductors.

Dynamics of the Magnetic Flux in Superconductors

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Funding:	$80,000

PROGRAM SCOPE

Superconductors have various applications because of their ability to conduct high electric currents without energy losses and to generate high magnetic fields. Studies of the dynamics of vortices are crucial for making progress in this area. Another important area of applications of superconductors comes from the Josephson effect that allows generation of microwave radiation and manufacture of sensitive magnetic field probes - SQUIDs. Flux qubits based upon Josephson tunneling junctions are considered among the most promising elements of quantum computers. The work on the DOE grant at Lehman College is advancing the knowledge of superconductors and their applications by answering fundamental and practical questions of the dynamics of magnetic flux in superconducting materials and circuits. Recent research topics include generation of acoustic and electromagnetic waves by the flux flow, ignition of vortices by ultrasound, decoherence of flux qubits by thermal phonons, and spin Hall conductivity in metals. Current research focuses on terahertz radiation from layered superconductors, nucleation of vortices by surface acoustic waves, coupled dynamics of vortices and dislocations moving under elastic stress, electric control of magnetic memory units, and spin Hall effect. Research is integrated with education through involvement of graduate and undergraduate students.

Theory and Computation for Semiconductor Catalysis and Solar Water Splitting

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Funding:	$140,000

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 $2H_2O \rightarrow 2H_2 + O_2$. 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 $Ga_{1-x}Zn_xN_{1-x}O_x$. 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 genetic structure-predicting algorithms in order to predict thermodynamically relevant surface and interface structures. We study the perovskite-structure polar materials of the $CaTiO_3/SrTiO_3/BaTiO_3$ family. Their interfaces with water offer new ways to tune the photochemistry.

FY 2012 HIGHLIGHTS

Progress is occurring on four projects. (1) The clean non-polar (10-10) surface of GaN has a complicated interaction with water. The first monolayer of water is predicted to split completely into Ga-OH and N-H entities bound to the surface. Adding additional water causes some of these split species to fluctuate into the various other species, including recombined H_2O. We will try to find out why this happens. (2) Surface structure prediction computer codes have been improved, and new candidate structures of several relevant surfaces are under study. (3) The atomically-relaxed GaN/ZnO bulk alloy configurations are being analyzed in detail. (4) The process of water oxidation on the $SrTiO_3$ (100) surface is being quantified.

Surface Electromagnetic Phenomena in Pristine and Atomically Doped Carbon Nanotubes: Fundamentals and Applications

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Funding:	$100,000

PROGRAM SCOPE

This theoretical project addresses fundamentals and applications of electromagnetic interactions in quasi-one-dimensional carbon nanomaterials. Ultra-fast quantum processes in pristine and atomically doped carbon nanotubes (CNs) are being explored in the near-field to learn how to control and reliably manipulate surface atomic, photonic, and excitonic states in these systems. The research program focuses on (1) physical properties of surface exciton-plasmon resonance excitations in pristine single wall CN systems; (2) properties of cavity polariton states in hybrid quantum systems composed of single wall CNs doped with single atoms, ions, or nanotubes coupled to semiconductor quantum dots; (3) exciton energy transfer in single wall CN bundles/films and their related optoelectronic properties. The emphasis is on getting a better understanding of underlying quantum phenomena and providing guidance for future experiments that might result in creation of new research subfields, such as carbon nanophotonics (as opposed to semiconductor nanophotonics) and carbon nanoplasmonics. The focus is on the development of a new generation of carbon based, high-yield, high-performance, tunable optoelectronic and sensory devices for use in solid state quantum information, quantum communication, energy conversion, and storage technologies.

FY 2012 HIGHLIGHTS

Pristine Carbon Nanotubes: We have shown theoretically that the non-radiative exciton-to-plasmon energy transfer, whereby the external electromagnetic radiation absorbed to excite excitons transfers into the energy of surface plasmons, can efficiently mediate and greatly enhance the electromagnetic absorption by pristine semiconducting carbon nanotubes. The strong local coherent fields produced in this way can be used in various new technological applications of carbon nanotubes, such as near-field sensing, optical switching, electromagnetic energy conversion, and materials nanoscale modification. [*Physical Review* B 85, 035448 (2012)]

Hybrid Carbon Nanotube Systems: Hybrid CN systems, nanotubes containing extrinsic atomic type species such as semiconductor quantum dots, extrinsic atoms, or ions, are promising candidates for the development of the new generation of tunable nanooptoelectronic devices—both application oriented (e.g., photovoltaic devices of improved light-harvesting efficiency) and devices for use in fundamental research (e.g., in the solid-state quantum information science). Here, by calculating non-linear optical response signals, we have shown that the bipartite entanglement of a pair of spatially separated two-level dipole emitters coupled strongly to a low-energy surface plasmon resonance of a metallic CN can be identified unambiguously through the presence of the cross-peaks in the 2D photon-echo spectra. [*Chemical Physics*, Special Issue on Nanotube Photonics, in print]

Theoretical Investigations of Nano Bio Structures

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Funding:	$100,000

PROGRAM SCOPE

This grant addresses fundamental issues in nanoscale science and technology, namely the design of nano- and bio-inspired materials and processes with desired, novel characteristics. The research focuses on several broad areas, including environmentally important enzymatic reactions, self-assembly mechanisms and structure evolution at surfaces, molecular devices, and multi-terminal junctions with novel characteristics. Methodology development is an important part of the research, enabling large-scale simulations of solvated systems, evaluation of free-energy barriers, and calculations of quantum interference effects in electron transport. Our real-space multigrid method is capable of simulating the dynamics of systems containing thousands of atoms on DOE's leadership-class massively parallel supercomputers.

CMCSN: Computational Time-Resolved and Resonant X-Ray Scattering of Strongly Correlated Materials

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Funding:	$320,000

PROGRAM SCOPE

Our Collaborative Research Team (CRT) will focus on developing viable computational schemes for modeling x-ray scattering and photoemission spectra of strongly correlated materials in the time-domain. The substantial arsenal of formal/numerical techniques and approaches encompassed by the members of our CRT will be deployed through appropriate generalizations and extensions to model the pumped non-equilibrium state and its dynamics and to determine how it can be probed via x-ray absorption (XAS), emission (XES), resonant and non-resonant x-ray scattering, and photoemission processes. Notably, there are conceptual connections between the time-domain problems and other second-order spectroscopies, such as resonant inelastic x-ray scattering (RIXS) because RIXS may be effectively thought of as a pump-probe experiment in which the incoming photon acts as the pump, and the fluorescent decay is the probe. This project will substantially advance the understanding of x-ray scattering processes in the time-domain as well as in the more conventional scattering channels, including time-resolved photoemission, and how such processes can be modeled realistically in complex correlated materials more generally. The modeling of relaxation processes involved in time-domain spectroscopies is important also for understanding photo-induced effects, such as energy conversion in photosynthesis and solar cell applications, and thus impacts the basic science for energy needs.

FY 2012 HIGHLIGHTS

(1) A non-equilibrium Keldysh formalism was used to study the time-resolved electron momentum distribution in pump-probe to show that the oscillations observed in the momentum distribution can be used to map dispersion of the unoccupied parts of band structure which are hidden to traditional equilibrium probes. (2) We studied non-equilibrium charge density wave (CDW) systems with focus on time-resolved photoemission to show the emergence of a new non-equilibrium paradigm, namely, the gap collapse while the CDW order remains. (3) The influence of a proposed circulating-current state on the dichroic signals in a number of x-ray spectroscopies was studied using small cluster exact-diagonalization to ascertain bounds on the strength of such a current in these experiments. (4) Using our newly developed small-cluster exact-diagonalization code, we found that low energy response in Cu L-edge RIXS experiments can be attributed to single-spin-flip excitations or spin waves, and compares quite well with the magnetic structure factor $S(q,\omega)$ modified by polarization dependent matrix elements even in doped cuprates. (5) We have continued to develop and test our *ab initio* RIXS code based on a real-space multiple-scattering Green's function formalism, implemented as an extension of the FEFF9 multiple scattering x-ray code. (6) We have extended calculations of RIXS and XAS spectra of cuprates to the intermediate coupling regime by implementing our recent GW approximation based scheme for the self-energies.

Electronic Structure, Spectroscopy, and Correlation Effects in Novel Materials

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Funding:	$261,000

PROGRAM SCOPE

This project concerns theoretical studies of electronic structure, spectroscopic response, and correlation effects in a wide variety of novel materials of current interest. Our overarching goal is to undertake realistic modeling of various highly resolved spectroscopies of materials for providing discriminating tests of competing theoretical scenarios and as a rational basis for future experimentation. We emphasize that spectroscopies do not provide a direct map of electronic states, but act as a complex ‘filter’ or ‘mapping’ of the underlying spectrum. This link between electronic states and the measured spectra—the ‘matrix element effect’—is in general extremely complex, but a good understanding of this link is crucially important for fully exploiting various spectroscopies. Accordingly, we are working toward formulating and implementing increasingly sophisticated methodologies for making direct connection with angle resolved photoemission, resonant inelastic x-ray scattering, scanning tunneling microscopy/spectroscopy, magnetic and non-magnetic Compton scattering, and positron annihilation spectroscopies, including some work on neutron scattering and optical spectra. Specific systems considered are cuprates, pnictides, topological insulators, manganites, magnetite, and nano-particles. Although LDA provides an important baseline, 'beyond LDA' schemes are invoked for modeling the underlying electronic spectrum in correlated materials in order to incorporate the physics of superconducting orders, pseudogaps, impurities and nanoscale heterogeneities, and how matrix element effects can enhance/suppress related signatures in various spectroscopies. This project thus aims to help fill a critical gap in the available tools for understanding, analyzing and interpreting a wide range of spectroscopies in use today, and to obtain through direct comparisons between theory and experiment new insights into electron correlation effects, Fermi surfaces, magnetism and related issues.

FY 2012 HIGHLIGHTS

(1) The first material realization of the semiconductor SnTe as a topological crystalline insulator was predicted. (2) We proposed that Weyl semimetal can be realized at the topological critical point in $TlBi(S_{1-x}Se_x)_2$ and $TlBi(S_{1-x}Te_x)_2$ alloys by breaking the inversion symmetry. (3) Doping dependent scanning tunneling spectra from Bi2212 were analyzed to show that our 'beyond LDA' comprehensive modeling scheme captures many salient features of the spectra. (4) Using the three-band Hubbard model of NCCO superconductor, we showed how the three critical [non-superconducting] energy scales of the cuprates—the Mott, charge-transfer, and pseudogap—appear in the RIXS spectrum. (5) Through a combined theory-experiment Compton scattering study, we showed the persistence of covalent bonding in liquid silicon. (6) By modeling and analysis of light scattering spectra from Li_xFePO_4 battery material, we showed that the spectra fingerprint the (de)lithiation process with rich information on Li distribution, valence, spin states, and crystal field.

Dynamics and Nonequilibrium Effects in Higher-Order and Pump-Probe X-Ray Spectroscopy

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

PROGRAM SCOPE

The beginning of the 21st century has seen an exciting increase in our ability to control materials at the quantum level, which could have an enormous impact on a wide array of critical technologies. Many phenomena related to quantum control, such as catalysis, photochemistry, photosynthesis, photoinduced effects, and device physics, require an understanding of the nonequilibrium dynamics underlying these physical processes. In order to characterize the dynamics in quantum systems, scientists are developing a wide array of experimental tools that have as a goal the measurement of the response of the structural and electronic properties of a material to an external stimulus, often an optical or terahertz pulse. Typical examples of photoinduced phenomena are insulator-to-metal transitions, magnetization and demagnetization, spin-crossover transitions, and melting of charge and orbital order. The typical timescale of the dynamics is of the order of picoseconds down to femtoseconds. The goal of the program is to lay a fundamental basis for the use of x-ray spectroscopy to study dynamics and nonequilibrium effects. This program theoretically investigates the use of time-dependent x-ray absorption and scattering in the study of dynamics and nonequilibrium phenomena, in particular, on strongly-correlated systems, such as transition-metal compounds.

FY 2012 HIGHLIGHTS

Fast intersystem crossing is an intriguing phenomenon that has puzzled many for several decades. In a wide variety of transition-metal complexes, laser excitation creates a photoinduced excited state that decays on the order of tens to hundreds of femtoseconds into a state with often a different spin and a significant change in transition metal-ligand distance. We provided an explanation for the ultrafast photo-excited electron dynamics in low-spin Ruthenium (II) organic complexes. The experimentally-observed singlet to triplet decay in the metal-to-ligand charge-transfer (MLCT) states contradicts the expectation that the system should oscillate between the singlet and triplet states in the presence of a large spin-orbit coupling and the absence of a significance change in metal-ligand bond length. This dilemma is solved with a novel quantum decay mechanism that causes a singlet-to-triplet decay in about 300 fs. The decay is mediated by the triplet metal-centered state (MC) state even though there is no direct coupling between the singlet MLCT and triplet MC states. These changes also have a large impact on x-ray spectroscopy. Dynamic x-ray absorption spectra were calculated for the first several hundreds of femtoseconds. Dramatic changes in the spectral line shape are observed that can be directly related to nonequilililibrium dynamics. More recently, we have made significant progress in the understanding of the photoinduced metal-insulator transition in vanadium dioxide. It can be shown that transition is due to the interplay between electron-electron scattering, the collapse of the insulating gap, and the lattice. Finally, we have worked on resonant inelastic x-ray scattering and x-ray absorption on iridates in collaboration with experimentalists working at the nation’s light sources.

Electronic Structure and Novel Properties in Complex Oxides and Hetero-Interfaces

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Funding:	$105,000

PROGRAM SCOPE

In this program, we explore various kinds of interfaces such as transition metal interfaces, metal-semiconductor interfaces and so forth. These interfaces possess rich physics including superconductivity, topological insulators, and electric-field driven magnetism. Theoretical or computational developments in electronic structure studies will provide an excellent tool for identifying striking phenomena as well as for guiding the exploratory synthesis of novel materials. We now focus on the elucidation of several striking, diverse, and challenging phenomenon observed in perovskite hetero-interfaces and semiconductor hetero-bonded interfaces. More specifically, we focus on (1) interface electronic structure and the possible excitonic mechanism of superconductivity in CuCl/Si superlattices; (2) tailoring of magnetism and magneto-crystalline anisotropy (MCA) of magnetic multilayers and interfaces via the application of external electric fields; (3) the search for a new class or type of topological insulators (TI), which include Bi2Se3-based, Pb-based chalcogenides, and halides;

(4) LaAlO3/SrTiO3 hetero-interfaces and their possible interface superconductivity; and (5) structure and magnetic order in bilayer manganites.

FY 2012 HIGHLIGHTS

First, in exploration for the excitonic mechanism of superconductivity, the code implementation of the Kernel function to evaluate the excitonic pairing has recently been done. Second, the role of an electric field at an interface of a transition metal and MgO interface has been studied, where monolayer Fe in the Fe/MgO interface gives rise to a perpendicular MCA and the electric field introduces some modification. Interestingly, the MCA of $Fe_{0.75}Co_{0.25}$/MgO is gigantically modified, where the existence of an FeO layer at the interface is mostly responsible for the resultant physics. Furthermore, possible switching by the electric field between out-of-plane and in-plane MCA at the Fe/MgO interface was also investigated. Third, we studied the recently discovered pnictide superconductor, SrPtAs, which is the first hexagonal structure without an Fe atom. In this material, large spin-orbit coupling at Pt drives an admixture of spin singlet and triplet. Despite the presence of the global inversion symmetry in SrPtAs, locally broken inversion symmetry at the PtAs layer exhibits properties of non-centrosymmetric superconductivity. Finally, we proposed new types of topological insulators: (1) by substituting O for the surface Se atom at the end of the Bi2Se3 film, an ideal Dirac cone emerges as a point-like Fermi surface, which reveals the tenability of a Dirac cone by O substitution; (2) Pb-based chalcogenide series, where superlattice of a certain type enhances TI properties, and (3) perovskite halides, where a combination of the large spin-orbit coupling and crystal field splitting results in TI properties.

Theory of Hydrogen Storage in Complex Hydrides

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Funding:	$260,000

PROGRAM SCOPE

We are developing a systematic, quantitative approach to designing novel materials with fast (de)hydrogenation kinetics using state-of-the-art first-principles density functional theory calculations based on microscopic models of nucleation, mass transport, and diffusion. One of our main objectives is to develop a comprehensive theoretical framework for describing the kinetics of phase transformations in multinary complex hydrides, including the nucleation and growth of product phases upon hydrogen release and uptake. This framework will fill a critical basic science area of need in the hydrogen storage field, providing an in-depth atomistic picture of the kinetics of phase transformations controlling the rate of hydrogen release from multicomponent complex hydrides.

The successful prediction of novel materials and reactions will also require development of more broadly applicable computational tools, which we are developing (1) computational prediction of crystal structures of new materials, (2) Monte Carlo methods to deduce stable interfaces (for nucleation kinetics), and (3) the use of high-throughput computation and data mining tools to elucidate descriptors for materials properties.

Modeling Dynamically and Spatially Complex Materials

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Funding:	$120,000

PROGRAM SCOPE

Our goal is to construct accurate classical potentials for metals and alloys to understand and predict mechanical behavior. Initially potentials are created for widely used bcc metals—V, Nb, Ta, Mo, W—and elements often used in alloys (Al and Ti to start).

Our approach uses public codes and public data at every stage. Density function theory (VASP with PBE) constructs a public database to which spline potentials are fit using public POTFIT code. The database contains well-converged snapshots of 100-500 atom supercell configurations chosen to cover the expected range of the potential. Each snapshot has the forces, energies per atoms, and stresses for the configuration resulting from the final step of a simulation. The public code POTFIT has been modified to achieve potentials of improved quality: EAM, MEAM and MEAM SW1 and MEAM SW2. The first two are established forms in the literature. The latter two are new to this work. Each fit is tested by comparing additional properties not in the fitting procedure with the DFT values. Perfecting these steps has taken several years. Now we are at production stage for the five bcc metals. In the future, we believe all the procedures can be used to produce alloy potentials. In any alloy, say V-Nb, we could use the existing potentials of elements (V and Nb) needing to fit only the additional terms associated with interactions between V and Nb.

Others could use potentials with public molecular dynamics code LAMPPS maintained at Sandia National Laboratory. We have posted code to generate forces from our spline-fit potentials. New potentials could be generated for problems working in a range not anticipated in our original fits. That could be done by others who generate the needed data with DFT and then employ our fitting procedures to obtain new potential.

FY 2012 HIGHLIGHTS

In 2010, we published EAM potential for niobium (Nb). The response caused us to add one high pressure snapshot to the fitting data. Now potentials for five bcc metals (V, Nb, Ta, Mo, W) exist in EAM and MEAM forms.

This is the first time EAM and MEAM potentials exist for the same database of the same element, let alone for two new forms. The expected usage is MD with EAM to get some idea of the running time and initial results. That MD may suffice for some needs, especially since these EAM potential are better fits than exist. In the case EAM results suggest important questions, investigators can use MEAM potential that will take more computing time.

Quantum Simulations of Orbitally Controlled Physics and Nanoscale Inhomogeneity in Correlated Oxides

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Funding: $120,000

PROGRAM SCOPE

The goal of this project is to develop a general theoretical framework to understand conductor-insulator transitions, both metal-insulator and superconductor-insulator transitions, driven by disorder. We focus on how the interplay of disorder with other parameters can lead to nanoscale inhomogeneity not only in the local density and local magnetization, but also in the local electronic structure probed by scanning tunneling spectroscopy and in the local frequency-dependent response functions. We also aim to develop state-of-the-art algorithms for (1) large scale matrix diagonalization using a modified Lanczos method and (2) the maximum entropy method constrained by sum rules for extracting frequency dependent functions from quantum Monte Carlo simulations. Both of these methods are necessary for addressing the full complexity of disordered, correlated, multi-orbital oxides and di-chalcogenides.

FY 2012 HIGHLIGHTS

One of our major highlights was to show evidence for Emergent granularity on the meso-scale across the superconductor-insulator transition and determine the energy scales in both phases. We used quantum Monte Carlo simulations that treat, on an equal footing, inhomogeneous amplitude variations and phase fluctuations, a major advance over previous theories.

Theoretical Investigations of Single Particle Spectroscopies of Novel Materials

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Funding: $105,000

PROGRAM SCOPE

Complex materials like transition-metal oxides exhibit a rich variety of phases and phase transitions. Their unusual properties, like high temperature superconductivity and colossal magnetoresistance, and their extreme sensitivity to small changes in external parameters suggest the potential for novel applications. The theoretical study of these materials is challenging because they are made up of strongly interacting degrees of freedom. Our goal is to gain theoretical insight into unusual behaviors of high Tc superconductors and CMR manganites, with special focus on their spectroscopic properties.

FY 2012 HIGHLIGHTS

The observation of quantum oscillations in underdoped cuprates has generated intense debate about the nature of the field-induced resistive state and its relation to the “normal" state of high Tc cuprate superconductors. Quantum oscillations suggest a Fermi liquid state at high magnetic fields H and low temperatures, in contrast to the high-temperature, zero-field pseudogap state probed by ARPES and other spectroscopies. Motivated by recent high-field heat capacity measurements, we present a theoretical analysis of the electronic excitations in a vortex-liquid state, with pairing correlations that are short-ranged in both space and time. We show that we can reconcile these seemingly contradictory experimental observations. We show that phase fluctuations that give insight into the pseudogap in the high temperature classical regime also lead to a large and singular density of states (DOS) suppression that goes like square-root H at low temperatures. In addition, the DOS shows quantum oscillations with a period determined by a Fermi surface reconstructed by a possible competing order parameter in the vortex liquid.

In a separate work, we theoretically investigate the effect of strain on half-doped manganites and show that one can tune the system to the proximity of a metal-insulator transition and thereby generate a colossal magnetoresistance (CMR) response. Using magneto-transport calculations within the Kubo formalism, we demonstrate that, under tensile strain, a ferromagnetic charge ordered insulator—previously inaccessible to experiments—becomes stable. The phase competition not only allows control of CMR in ferromagnetic metallic manganites but also generates CMR response in otherwise robust insulators at half doping.

Change, Spin and Heat Transport in Low-Dimensional Systems

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Funding:	$90,000

A summary for this program was not available at press time.

Theory of Topological Quantum Numbers in Low Dimensions

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Funding:	$125,000

PROGRAM SCOPE

Emergent properties that are robust to external disturbances, such as magnetization, have bearing on both our understanding of fundamental physics and technology. Of great interest in recent years have been the so-called topological quantum phases of matter, which do not possess long-range order but are characterized by certain quantum numbers that are invariant to weak continuous perturbations. Such phases reveal a new paradigm for collective behavior and also hold the promise of a profound impact on future technology, such as topological quantum computation. A great deal of experimental work is going on at Penn State on topological insulator materials.

This proposal aims to examine a variety of physical phenomena that are believed to have topological origin, with a view to determine the range of applicability and the robustness of the topological behavior. The best known such phase of matter is the fractional quantum Hall effect, observed when electrons are confined to two dimensions, cooled to near absolute zero temperature, and exposed to a strong magnetic field. It is believed that quantities such as the quantized Hall resistance, fractional charge, effective magnetic field, edge Luttinger liquid exponent, and abelian and nonabelian braid statistics are topological in nature; but robustness to continuous perturbations has not yet been confirmed for all of these quantities. A significant fraction of the current proposal concerns the nature of the 5/2 and other fractional quantum Hall states in the second Landau level that are believed to support excitations with nonabelian or more complex braid statistics. The possible role of Landau level mixing in establishing such phases will be investigated, as will be the effects of disorder and the spin degree of freedom. The second major thrust will be the newly discovered three-dimensional topological insulators, which, unlike ordinary insulators, possess conducting surface states with unusual properties. The proposed work will focus on the effect of their coupling to a ferromagnetic, antiferromagnetic, or superconducting overlayer, the influence of a magnetic field, and the consequences of geometrical confinement at the nanoscale. A combination of numerical and analytical methods including standard many body theory, Monte Carlo, exact diagonalization, and quantum field theory will be employed. The results of these studies are expected to be of direct relevance to numerous ongoing experimental studies.

Electronic and Piezoelectric Phenomena in Nanostructures

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Funding:	$110,000

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 electomechanical applications. Specifically, we propose to 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 2012 HIGHLIGHTS

We have obtained important results on two problems in Dirac materials.

(1) 3D Dirac Semimetals: 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 its critical point. Instead, our work identifies particular space-groups that allow three-dimensional Dirac points as robust symmetry protected degeneracies in the bulk. We identified a specific candidate material with the appropriate symmetry that we predict will realize this physics.

(2) Twisted Multlayer Graphene: Multilayer graphenes that grow in a rotationally faulted pattern show a collapse of the energy scale for interlayer electronic motion and are often regarded simply as a stack of independent graphene sheets. The microscopic basis for this layer decoupling is being vigorously studied. We examined the electronic spectra of rotationally faulted graphene bilayers within a continuum formulation appropriate for small fault angles and discovered that the coupled system can exist in either of two topologically distinct electronic states. One of these states shows a symmetry protected decoupling of its layers in a region in reciprocal space where its Dirac cones merge. Our results highlight the use of interlayer coupling as a robust mechanism for engineering the Dirac point topology in these materials.

First-Principles Investigations of the Physics of New Semiconducting Ferroelectrics for Solar Light Absorption and Carrier Separation

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Funding:	$250,000

PROGRAM SCOPE

This research program develops first-principles electronic structure methods to discover new single-phase (easy to synthesize) materials composed of earth-abundant elements that absorb visible light and separate the resulting carriers well. This combination of simple synthesis and efficient solar performance has proven elusive despite decades of research. In many cases, the carrier separation has been achieved by charge injection or other interface between two materials, most famously the silicon p-n junction. Materials without inversion symmetry can separate carriers throughout the bulk, simplifying photovoltaic material fabrication. However, many materials that exhibit a bulk photovoltaic effect either do not separate carriers well enough or do not absorb enough visible light.

Ferroelectric oxides are a promising category of materials for photovoltaic applications. They offer high electric polarization, and demonstrated ability to separate carriers. However, nearly all ferroelectric oxides are insulators, making them inefficient for solar photovoltaic applications.

We pursue three complementary research directions to develop low-band gap ferroelectric semiconductors. (1) We investigate the physics of carrier separation in ferroelectric oxides, calculating the main contribution to bulk photovoltaic effect from first principles for various recently-proposed ferroelectric oxides and other noncentrosymmetric semiconductors. (2) We investigate ferroelectric and other highly polar oxide and oxide-related materials computationally. Ordered and disordered solid solutions, intergrowth structures, and other material combinations are examined with first principles calculations. (3) We study the known semiconducting materials for the purpose of investigating whether ferroelectricity can be induced in them, through strain, contact with a polar material, or other material modification strategy. Our research provides an understanding of connections between material composition, arrangement, and functional responses including light absorption and carrier separation.

This research program is geared toward the materials design and discovery of new photovoltaic materials that are inexpensive and efficient. This will reveal how to arrange matter to provide strong light absorption and carrier separation in inexpensive materials. Therefore, our program of theoretical condensed-matter physics and computational materials design can lead to the discovery of new efficient solar photovoltaic materials, for next-generation solar devices.

FY 2012 HIGHLIGHTS

We have computationally designed perovskite solid solutions that can be synthesized by conventional solid-state route and exhibit stable room-temperature ferroelectricity, and a low, direct band gap comparable to that of the Si and CdTe semiconductors used in current photovoltaic. These properties, as well as the fact that the solid solution consists of inexpensive elements, make this material a promising candidate for use in solar energy devices.

In collaboration with experimental colleagues, we have examined optical switching of ferroelectric polarization of $PbTiO_3$. We observed a photo-induced, large amplitude polarization increase in the prototypical ferroelectric $PbTiO_3$. This modulation is driven by the motion of photo-generated free charges in the internal field of the ferroelectric and corresponds to an ultrafast, optically initiated bias. The observed photo-generated current is predicted by our first-principles calculations.

Studies of the Marginally Jammed Solid

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Funding:	$120,000

PROGRAM SCOPE

A perfect crystal is the essence of order; in a well-defined way, a collection of spheres at the jamming transition is the epitome of disorder. Our work has shown that this jamming transition is singular in that there is a diverging length scale that appears at the transition. This length scale is due to the fact that the number of inter-particle contacts at the transition is exactly the minimum number needed for mechanical stability. This singularity controls the harmonic as well as the anharmonic properties of the solid in the vicinity of the transition. Our project addresses the following questions: (1) *How does the system behave when pushed beyond the harmonic regime so that anharmonic effects become important?* We have shown that the most anharmonic vibrational normal modes are at low-frequency where they are quasi-localized. These modes are exquisitely sensitive to stress or temperature because they have low energy barriers to particle rearrangements. *Can these modes be used to predict where local failure might occur?* At the jamming transition, anharmonic effects diverge. *How do they evolve as the system is compressed above that transition? Can we predict from the anharmonic response how* *close a system is to the edge of failure?* (2) *What is the effect of temperature? Could the anharmonic quasi-localized modes be responsible for phenomena associated with the glass state, such as the excess number of excitations, or dynamical heterogeneities that appear as the glass transition is approached? In particular, how is the jamming transition related to the glass transition?* (3) *How do generalizations of the model, such as non-spherical particle shapes, attractive interactions, and three-body interactions, affect the picture developed for idealized spheres?*

FY 2012 HIGHLIGHTS

We analyzed the finite-size effects in jammed packings of soft, frictionless spheres at zero temperature and found that the contact number and elastic moduli exhibit scaling collapse with a nontrivial scaling function. This demonstrates that the jamming transition is a phase transition with an upper critical dimension of 2. We are extending the “soft spot” analysis to explore the connection between soft spots and (1) dynamical heterogeneities above the glass transition, (2) rearrangements that occur during aging in thermal systems below the glass transition temperature, (3) rearrangements that occur at nonzero shear rates, and (4) dislocations in crystalline systems. Collectively, these studies explore the robustness and generality of the soft spot description of flow defects in solids. Finally, we have developed a protocol to continuously tune a system from perfect order to complete disorder. Many of the properties of the jammed solid are dominant and persist throughout nearly the entire range of order.

CMSN: Structure and Dynamics of Water and Aqueous Solution in Materials Science

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Funding:	$145,000

PROGRAM SCOPE

The goal of this project is to understand the structure and the spectroscopy (IR, optical, x-ray, and neutron) of liquid water from ab-initio quantum mechanical theory. This grant partially supports research towards this goal at Princeton University, at UC Davis, and at the University of Washington. In addition, the grant stimulates debate and collaboration within a wider network comprising more than 30 theorists and experimentalists associated with other US universities, national laboratories, and major international research institutions. The program initiated with a kickoff workshop held at the Princeton Center for Theoretical Science on December 6-8, 2010. The second workshop of the series took place at the Talaris Conference Center in Seattle on February 10-12, 2012. A third workshop will be held at UC Davis in June 2013 at the end of the funding period.

FY 2012 HIGHLIGHTS

Research conducted at Princeton University showed that correlated proton tunneling occurs in the low temperature quantum phase transition from ice VIII to ice VII. Quantum correlation is signaled by the entanglement spectrum of the single particle density matrix associated to the protons.

In collaboration with experimental teams in Italy and the U.K., the Princeton group carried out an analysis of new deep inelastic neutron scattering, probing the spherical momentum distribution of the protons in hexagonal ice. The study made use of new theoretical concepts introduced by the Princeton group in the previous funding period to extract the mean force experienced by the proton from the experimental Compton profile.

New calculations of the x-ray absorption spectra of liquid water under ambient conditions and of hexagonal ice close to melting were reported using a static GW approach developed by the group. This study found that including inhomogeneous effects in the screening and quantum disorder in the proton configurations was essential to bring the theory in close agreement with experiment, so that the spectral differences between water and ice observed in experiments could be reproduced quantitatively in the calculations. This study indicated how the x-ray absorption and Raman scattering features reflect the changes in the H-bond network occurring upon melting/crystallization of water.

Fundamental Theory of Electronic Structure in the Nanoregime: Transport through Single Molecules

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PROGRAM SCOPE

The goal of this project is to provide a framework for realistic calculations of electronic properties and of transport in nanoscale structures such as molecular wires suspended between metallic electrodes. Current work at Princeton is focused on the implementation of the GW formalism to molecular conduction, as this approach should improve substantially the electronic level alignment. Our approach should allow realistic calculations of the transport characteristics of devices consisting of hundreds of atoms in the context of quasi-particle theory. Research effort has also been devoted to include a realistic treatment of van der Waals interactions in density functional calculations of atomistic structures.

FY 2012 HIGHLIGHTS

In collaboration with a group at the Fritz Haber Institute in Berlin (Germany), the Princeton group has developed an efficient method to treat many-body effects in van der Waals (vdW) interactions. This study showed that screening and many-body vdW interactions are essential for an accurate treatment of conformational energies of biomolecules and molecular binding in nanodevices.

The group developed a novel scheme to compute the electron self-energy at the static GW level including a full treatment of screening at the RPA level. The approach is currently tested in spectral calculations for bulk crystals and liquids but will soon be applied to describe the level alignment at nanodevices for single molecule electronics.

Internal Geometry, Stability and Design of Quantum Hall States

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Funding:	$475,000

PROGRAM SCOPE/FY 2012 HIGHLIGHTS

In the early 1980s, measurements on a two-dimensional layer of electrons sandwiched between two semiconductors in a perpendicular applied magnetic field led to the discovery of a fundamental new state of electronic matter: the fractional quantum Hall effect (FQHE), in which the charge of the electron was fractionalized. In the intervening 30 years, families of new states have been discovered, variously dubbed incompressible quantum Hall liquids, striped and bubble phases, and Abelian and non-Abelian states. While there has been considerable theoretical progress using a combination of inspired guesses of the quantum many-electron wavefunctions, as well as numerical studies of small systems, there remain major gaps in our understanding.

Our team's coordinated effort in the past funding period has yielded many new results. First, Haldane uncovered a previously unrecognized degree of freedom—a shear deformation, which is a special case of an area-preserving diffeomorphism—possessed by incompressible fractional quantum Hall states. This was discovered as the team studied systems without rotational symmetry, e.g., systems with anisotropic mass, or under a magnetic field that is not normal to the two-dimensional plane. The ensuing investigation has yielded answers to many surprising results that apply to the FQHE. In parallel, intensive numerical studies yielded several new results for non-Abelian states. In graphene-based chiral materials, we realized the ability to tune through different incompressible and compressible states in a single Landau level, and found the right experimental parameters for the exploration of universal Luttinger liquid behavior, heretofore not obtained in semiconductor based electron systems.

We seek to build upon the new discovery and understand its implications for multi-component anisotropic systems, inhomogeneous systems, and systems in confined geometries with boundaries, as well as composite fermion Fermi liquid states. We plan to extend our investigations to other anisotropic systems and to seek systems with new, interesting phase diagrams in the quantum Hall regime, with an eye to optimizing the stability of various phases. We propose also to extend our study to cold atom based systems.

In parallel, we will perform controlled, systematic numerical studies on various fronts, again towards the purpose of achieving a fuller, quantitative understanding of the nature and stability of the more fragile quantum Hall states. Many quantum Hall phases require reliable studies on larger sizes than is possible with exact diagonalization. Based on preliminary studies, we have identified the optimum geometry for the use of the Density Matrix Renormalization Group method, to extend the size of systems that can be studied for reliable extrapolation to the thermodynamic limit. Further, we will use a real-space entanglement method to study the topology and entanglement spectrum of various quantum Hall states.

Predictive Computing for Condensed Matter

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Funding:	$150,000

PROGRAM SCOPE

Predicting the properties of strongly correlated electronic systems from first principles, such as high temperature superconductors and quantum magnets, is not only key to answering pressing material questions of our time but is amongst the central intellectual challenges in computational condensed matter physics. So far, almost all understanding has been obtained from very simplified models where the atomic degrees of freedom are lost. In this work, we focus both on fundamental new algorithmic developments in dynamical mean-field theory, density matrix embedding, and infinite density matrix renormalization group, as well as their realization on very large-scale scientific computing architectures, to move the discussion and understanding of strongly correlated materials forward from models to predictive atomistic Hamiltonians.

FY 2012 HIGHLIGHTS

In the few months that this project has started, we introduced several new advances. The first was a way to obtain excited states and Green's functions from full configuration interaction quantum Monte Carlo, hitherto considered a ground-state method only. This gives a new route to obtain spectral functions for use in dynamical mean-field theory calculations. Second, we have published our work on density matrix embedding theory. This is a simple competitor to dynamical mean-field theory, which allows us to compute similar quality results at a fraction of the cost. The key intellectual advance in density matrix embedding is to abandon the frequency-dependent Green's function for the single-particle density matrix, and thus to move from a self-energy based embedding formalism to one which explicitly considers entanglement. The much lower cost of the density matrix embedding theory is already allowing it to be applied to much more complex models than have been considered so far in dynamical mean-field theory, including material Hamiltonians with all the long-range interactions. Taken together, these two advances form the first step on our path to understand correlated materials from first principles.

TMS: Defect Modeling Beyond Density Functional Theory

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Funding: $300,000

PROGRAM SCOPE

The goal of this project is to develop computational capabilities for accurate predictions of defect properties and to apply these developments to investigate the role of active defects in materials. We brought together a unique combination of people and expertise to tackle the problem: a forefront first-principles defect modeler with deep "field-specific" knowledge (S. Zhang), an expert in developing and applying "beyond DFT" methods for quasiparticle and optical excitations (P. Zhang), an expert in developing and applying quantum Monte Carlo (QMC) calculations for chemically accurate total energy calculations (J. Grossman), and an expert in developing mathematical models for applied physics (W. E). We carry out these computational and theoretical advances in the context of a set of outstanding energy-related problems, including impurities and defects in wide-gap oxides, doping limits, interfacial defects between highly dissimilar materials, and impurity diffusion.

FY 2012 HIGHLIGHTS

Density functional theory (DFT) within local approximation is a major theoretical tool for the study of defects. However, the results suffer from the often too-small DFT band gap. Recently, we showed that an important source of errors originates from the incorrect representation of the Fermi level of bulk materials, which can be corrected by using experimental ionization energy. Not only is this an important correction for DFT, the same correction should also be applied to post-DFT methods such as the hybrid functional methods [D. West, Y. Y. Sun, and S. B. Zhang, "Importance of the correct Fermi energy on the calculation of defect formation energies in semiconductors," Appl. Phys. Lett. 101, 082105 (2012)].

Topological insulator (TI) is a new class of matter with potential applications in electronics, spintronics, and quantum computing. We have carried out a series of studies for defects in TIs, which include how to tune Fermi level to the Dirac point by an exotic transfer doping method, the identification of atomic registry and STM images of transition metal impurities, and the effect of spin-orbit coupling on active native dopants [Y. Jiang, et al., "Fermi-level tuning of epitaxial Sb_2Te_3 thin films on graphene by regulating intrinsic defects and substrate transfer doping," Phys. Rev. Lett. 108, 066809 (2012); D. West, et al., "Identification of magnetic dopants on the surfaces of topological insulators: Experiment and theory for Fe on $Bi_2Te_3(111)$," Phys. Rev. B 85, 081305(R) (2012); D. West, et al., "Native defects in second-generation topological insulators: Effect of spin-orbit interaction on Bi_2Se_3," Phys. Rev. B 86, 121201(R) (2012)].

Atomistic Study of Ultrafast Dynamics in Multifunctional Materials in Bulk and Nanoforms

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Funding:	$135,000

PROGRAM SCOPE

The terahertz (THz) range of frequencies is borderline between microwave electronics and photonics. It corresponds to the frequency bands of molecular and lattice vibrations in gases, fluids, and solids. The importance of the THz range is in part due to rich fundamental physics associated with interaction of the matter with such radiation and in part due to numerous potential and emerging applications. However, the THz region is still poorly understood and underutilized nowadays. It is, therefore, timely and necessary to direct scientific and engineering efforts towards filling up the “THz gap.”

The ultimate goal of this proposal is to explore the fundamental terahertz, or ultrafast, dynamics of dipolar materials, such as ferroelectrics and magnetoelectrics, at both macro- and nano-scales through state-of-the-art computer simulations. To reach this goal we propose a focused comprehensive research effort with the following objectives: (1) develop a set of computational tools that allows accurate modeling of THz properties of ferroelectrics and magnetoelectrics at an atomistic level; (2) explore, predict, and understand the fundamental dynamical properties of ferroelectrics and magnetoelectrics at THz using our new simulator; and (3) explore, predict, and understand the physical response of multifunctional nanoscale materials to ultrafast external excitations.

FY 2012 HIGHLIGHTS

We have developed a computational approach to study ferroelectrics with inhomogeneous polarization distribution. We have studied ultrafast polarization reversal in ferroelectric nanowires and revealed competition between two polarization reversal mechanisms. We have developed a novel route to parametrization of force-fields in ferroelectrics which allows simultaneously accurate description of static and dynamics properties in such materials. Such force-field was used to reveal the existence of order-disorder component of the phase transition in classic displacive ferroelectric PbTiO3. We have reported the existence of giant elastocaloric effect in ferroelectric alloys and studied electrocaloric effect in some ferroelectric alloys. These lead to a computational discovery of coexistence of positive and negative electrocaloric response in such materials.

Quantum to Classical Crossover of Collective Modes in Correlated Matter

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Funding:	$91,000

PROGRAM SCOPE

Transient and long time properties of quenched quantum systems have given rise to a wealth of theoretical activity as well as experimental applications. A combination of numerical methods and conformal field theory has been crucial to their understanding.

The phenomenology of intermediate time behavior is potentially even richer, and often involves crossovers between different physical regimes, such as weak and strong coupling in the Kondo model. These crossovers are related to, but different from, other crossovers in out of equilibrium physics, such as those taking place when voltage or gate voltage are varied in tunneling experiments.

While potential applications are numerous, the subject is not fully developed theoretically. In particular, the methods of conformal field theory apply only in very special cases; and therefore new, more involved approaches are needed. In this project, we develop such approaches by using ideas of integrability—in a nutshell, developing further the ideas of Bethe ansatz out of equilibrium. These ideas will be combined with different numerical techniques—exact diagonalization and t-DMRG—and used to investigate a variety of interesting physical problems, such as non equilibrium transport through quantum point contacts.

Thermomechanical Properties of Thin Films and Membranes of Functionalized Nanocrystals and Nanowire Arrays: Multimillion-to-Billion Atom Simulations

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Students:	1 Postdoctoral Fellow(s), 2 Graduate(s), 1 Undergraduate(s)
Funding:	$180,000

PROGRAM SCOPE

This project focuses on thermomechanical properties of a new class of thin films and membranes consisting of functionalized nanocrystals and nanowires. We perform multimillion-to-billion atom reactive molecular dynamics (RMD) simulations based on quantum mechanically informed force fields to investigate interfacial structure and thermomechanical properties including adhesion and delamination, viscoelastic/viscoplastic behavior, and fracture in hybrid systems consisting of thin films and membranes embedded with nanocrystals and core/shell nanowires that are functionalized with organic molecules. Our recent quantum molecular dynamics (QMD) simulations have revealed atomistic mechanisms of rapid hydrogen production by aluminum nanoclusters in liquid water. We are currently performing RMD simulations to identify atomistic mechanisms underlying the remarkable ability of silicon carbide nanoparticles to heal surface cracks, which could help sustainable deployment of high-temperature materials for energy applications such as power generation systems.

FY 2012 HIGHLIGHTS

(1) Quantum Dynamics Simulations H_2 Production from Al nanoparticles in Water

We have carried out QMD simulations to investigate atomistic mechanisms of molecular hydrogen production by Al_n (n = 12 or 17) in liquid water. We have found a new mechanism with low activation barrier, in which a hydrogen molecule (H_2) is produced from a water molecule adsorbed at a Lewis acid site and hydrogen adsorbed at a Lewis base site on the cluster surface.

More recently, we have performed QMD simulations of Al_n (n = 16-18) in liquid water in order to investigate: (1) the role of a solvation shell formed by non-reacting H-bonds surrounding the H-bond chain and (2) the high size-selectivity observed in gas-phase Al_n-water reaction persists in liquid phase. The simulation results show that the solvation shell plays a crucial role in facilitating proton transfer and hence H_2 production. Namely, it greatly modifies the energy barrier, generally to much lower values. We have also found that the H_2 production by Al_n in liquid water does not depend strongly on the cluster size, in contrast to the existence of magic numbers (e.g.*,* n = 17) in gas-phase reaction experiments.

(2) Self-healing Ceramic Composites

We are performing and will continue to perform multibillion-atom molecular dynamics (MD) simulations and multimillion-to-billion atom RMD simulations of nanostructured materials under extreme environments to identify atomistic mechanisms of self-healing. We are performing 10^8-atom MD simulations to study fracture of Al_2O_3 embedded with 18 volume % of SiC nanoparticles under uniaxial tension. We use an environment-dependent interpolation scheme to combine the interatomic potentials developed by our group for SiC, SiO_2 and Al_2O_3.

To perform larger MD simulations of realistic nanostructures, we have recently benchmarked 10^{12}-atom MD simulation on the 163,840-core IBM BlueGene/P computer at the Argonne Leadership Computing Facility (ALCF) and are discussing with the ALCF Science Director, Paul Messina, the performance of multibillion-atom production runs for long trajectories on the new 786,432-core BlueGene/Q at Argonne.

Strongly Correlated Electron Systems

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Funding:	$70,000

PROGRAM SCOPE

One goal of the proposal is to understand the effects of inter-particle interactions on strongly correlated materials (containing elements from the lanthanide or actinide series) which typically exhibit a competition between magnetic and non-magnetic phases. We intend to discover mechanisms through which the systems can adapt to the competition, thereby producing novel phases with highly unusual properties. We examine the effects that the correlations in these phases have on the low-energy quasiparticle excitations, such as the emergence of heavy quasiparticle bands, the development of pseudogaps in the electronic excitation spectrum, and also their manifestations through thermodynamic and spectroscopic measurements. A second goal is that of examining the excitations of non-linear and non-ergodic lattices. This includes the determination of mechanisms which produce the phonon anomalies observed in uranium and plutonium compounds, and the appearance of localized modes of vibration which are of essentially non-linear character.

FY 2012 HIGHLIGHTS

We have discovered a mechanism that solves the 25-year-old question of "*What is responsible for the Hidden Order phase transition in URu2Si2, and what is the nature of the order parameter?*" We have shown that the spin-flip terms of the Hund's rule exchange can produce a combined spin and orbital density wave that gaps most of the Fermi-surface, produces an entropy change of about 0.3 kB ln 2 per uranium atom, and results in phase with broken spin-rotational invariance without producing any ordered magnetic moment. The order-parameter is difficult to detect since it requires a probe that is both sensitive to the spin and orbital characters.

Scalable Computational Tools for Discovery and Design: Excited State Phenomena in Energy Materials

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Funding:	$851,000

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. Our approach is based on advanced algorithms and many-body perturbation theory to facilitate the *ab initio* calculations and prediction of quasiparticle excitations and lifetimes, optical spectra, excited-state energy surfaces, transport properties, and other excited-state properties/processes. We will employ a unified approach that will describe simultaneously complex ground state structures and excited state phenomena.

Our methodology and algorithm development efforts are based on two of the most advanced and accurate approaches in materials research. Excited-state properties will be addressed in an interacting Greens 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.

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.

The funding shown is for all institutions.

Theory of Functionalized Nanostructures

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Funding: $120,000

PROGRAM SCOPE

The theme of our 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 to use are those composed of electronic materials, e.g., silicon. Within the nano regime, phenomena occur that are characteristic of neither the atomic limit nor the macroscopic limit. Such phenomena can have direct consequence for understanding and characterizing the electronic optical and magnetic 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 our 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, with particular emphasis on the role of dimensionality and quantum confinement.

Our proposed areas of research will enhance our understanding of nanomaterials and the role of quantum confinement and dimensionality at the nanoscale.

FY 2012 HIGHLIGHTS

The synthesis of fused quantum dots offers new possibilities for the design of nanoscale devices. We considered semiconductor quantum dots, fused along zinc-blende crystal directions, to construct nanomaterials systematically in one, two, and three dimensions. We solved for the electronic structure of such fused dots and outlined the potential use of these nanostructures for electronic applications. We also examined mechanical and electronic properties for germanium nanowires and considered the application of uniaxial strain on the nanowires. We calculated the Young's modulus for each wire and discussed the size and the nature (direct or indirect) of the band gaps as a function of growth direction, wire size, and strain. One of our most ambitious projects was to examine how Schottky barriers evolve a metal semiconductor interface. We considered a prototypical system of unprecedented size for a Pb(111) film on a Si(111) substrate. We considered more than 1,500 atoms and explicitly modeled the atomistic details of the interface. We found a pinning mechanism that depends critically on the role of quantum confinement and structural relaxation in the metallic film. We resolved a fundamental question of the applicability of the two standard theoretical descriptions from Schottky and Mott, and Bardeen. By changing the thickness of the overlying film, we find valid regions for both descriptions. This was an unexpected result.

Transport and Collective Properties of Semiconductors and Graphene Overlayers

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Funding: $205,000

PROGRAM SCOPE

We propose a theoretical research program on transport and collective properties in multilayers and nanostructures of diluted magnetic semiconductors. Despite tremendous progress on spintronics based on metallic ferromagnets, mostly marked by the success of read-out heads based on metallic giant-magnetoresistance trilayers, the greatest potential of spintronics lies in magnetic semiconductors, which can be more easily manipulated by adjusting gate voltages and doping profiles. In describing the transport properties of these systems, particular attention will be paid to anomalous terms in the semiclassical dynamics of electrons, which are usually neglected but are manifest in magnetic semiconductors where time reversal symmetry is broken. They are also important in nonequilibrium transport in non-magnetic materials and in nanostructures where space inversion symmetry is absent. In addition to this novel quasiparticle physics, we will investigate collective effects manipulated by external fields to affect the transport and optical properties, for example, to the magnetization orientation. We will include in our research scope the transport properties of Carbon nanotubes as well as magnetic and nonmagnetic semiconductor quantum wires, where the electrons form Luttinger liquids rather than Fermi liquids and physical properties are dominated by collective charge and spin excitations. Finally, as part of this project, we will develop a flexible density-functional formalism, compatible with multi-band envelope function descriptions of semiconductors. This tool will aid our investigations of ferromagnetic semiconductor nanostructures, and we expect it to enhance all theoretical work on inhomogeneous systems of interacting valence band holes.

FY 2012 HIGHLIGHTS

Much progress has been achieved in isolating graphene and a variety of different few layer graphene systems, in learning how to efficiently grow large area systems, and in understanding the unique electrical, magnetic, and chemical properties of these two-dimensional electron systems. More recently, researchers have identified three-dimensional topological insulator materials which have topologically protected surface states with electronic properties that are very close to those of graphene.

We have been exploring Berry phase physics for many years and recently have been applying this experience to the study of graphene and topological insulator systems.

Many-Body Effects in Chiral Electron Transport

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Sr. Investigator(s):	
Students:	1 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding:	$0.00 (Research was supported with prior fiscal year funding.)

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 in 2004-2005 to study spin Hall effect was subsequently applied to the problem of optical conductivity in graphene, within the scope of this project. The PI was the first who pointed out (in 2008) that the interaction corrections to the optical conductivity are suppressed by roughly two orders of magnitude despite the largeness of the coupling constant. This spectacular prediction led to an earlier vigorous debate at workshops and seminars and in publications (Herbut, Juricic, Vafek, 2008, 2010) before being accepted by the theorists (Sheehy, Schmalian, 2009; Sodeman, Fogler, 2012), and is in agreement with multiple experiments (Basov et al, Geim et al, Heinz et al, 2008). 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 2012 HIGHLIGHTS

We have studied the limit of infinitely strong impurities (e.g., adatoms) in graphene and the distribution of induced density around them. This density, via Coulomb interaction, is expected to modify the interaction between adatoms in graphene, predicted to be strong and long-range. We also considered formation of localized states induced by the Anderson impurity in bilayer graphene and its sensitivity to the interlayer bias, which opens up a possibility of gate control of the in-gap states.

Non-Equilibrium Relaxation and Aging Scaling of Magnetic Flux Lines in Disordered Type-II Superconductors

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Funding: $150,000

PROGRAM SCOPE

Technical applications of type-II superconductors, especially high-Tc compounds, 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. In our work, we aim for a thorough numerical investigation and theoretical characterization of the stochastic fluctuations and out-of-equilibrium relaxation processes of interacting magnetic flux lines subject to various pinning centers.

FY 2012 HIGHLIGHTS

Our studies have yielded considerable progress in our understanding of physical aging phenomena in type-II superconductors with uncorrelated point disorder, and revealed distinct intriguing temporal regimes that could be addressed separately in different sample and defect geometries. To this end, we employed a versatile three-dimensional Monte Carlo simulation code based on an elastic string representation of the magnetic flux lines, and extracted various steady-state observables as well as two-time correlation functions. Recently, we have developed an efficient Langevin molecular dynamics algorithm and validated both numerical approaches through a comparison of the ensuing long-time, large-scale stationary state characteristics. We are now investigating in detail 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.

Electron Interaction Effects in Nanosystems

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Funding: $140,000

PROGRAM SCOPE

This program aims to investigate effects of electron-electron interactions on the transport and thermodynamic properties of low-dimensional electronic systems (i.e., carbon nanotubes, single atom carbon chains, granular and homogeneously disordered superconductors, and superconducting single electron devices). This includes the study of (1) influence of equilibration of electron fluid on the transport properties of high mobility nanosystems, (2) electron correlations in single atom carbon chains, (3) boundary effects in the thermodynamic and transport properties of quantum dots based on armchair nanotubes, (4) resistance of p-n junctions in armchair nanotubes due to umklapp processes and electron-phonon processes, and (5) transport phenomena in SNS junctions with p-wave superconductors.

FY 2012 HIGHLIGHTS

(1) Theory of equilibration and hole dynamics in strongly interacting one-dimensional liquids. Although electron-electron (e-e) collisions conserve electron momentum, because of correlations between electron-impurity (e-i) and e-e collisions, they do affect transport properties of electronic systems. If the rate of e-e collisions is sufficiently fast, electron liquid equilibrates quickly and transport in clean semiconductor nanostructures may be described using the hydrodynamic approach. In a one-dimensional system, equilibration requires scattering of a high energy hole excitation across the bottom of the conduction band. Such processes cannot be described by the Luttinger liquid theory. Together with K. A. Matveev, the PI has developed a theory of equilibration of one-dimensional liquids at arbitrary interaction strength between the particles. This theory is relevant for electron transport of high mobility quantum wires. The results have been published [K. A. Matveev, and A. V. Andreev, Phys. Rev. B 85, 041102(R) (2012); K. A. Matveev, A. V. Andreev, and M. Pustilnik, Physica B: 407, 1898 (2012); K. A. Matveev and A. V. Andreev, Phys. Rev. B 86, 045136 (2012)].

(2) Manifestations of electron interactions in photogalvanic effect in chiral nanotubes. The PI developed a theory of photogalvanic effect in chiral carbon nanotubes in the regime where electrons form a strongly interacting quantum liquid. Correlations produce singularities in the dependence of the photocurrent on the frequency of the ac-pumping. The results have been published [R. Matthews, O. Agam, A. Andreev, and B. Spivak, Phys. Rev. B 85, 195430 (2012)].

(3) Electromagnetic propulsion and separation by chirality of nanoparticles in liquids. Magnetic nanoparticles can be separated by chirality from a racemic suspension in a liquid by using ac electromagnetic fields. Together with B. Spivak and E. Kirkinis, the PI constructed a theory of such separation. We identified a new mechanism of such separation, which relies on the existence of the intrinsic angular momentum of electrons in ferromagnetic particles. The results have been published [Kirkinis, A. V. Andreev, and B. Spivak, Phys. Rev. E 85, 016321(2012)].

Next Generation Photon and Electron Spectroscopy Theory

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Funding:	$150,000

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 complementary first principles methods, e.g., real-space multiple-scattering and Bethe-Salpeter equation techniques. These methods include many-body effects such as inelastic losses, core-hole interactions, vibrations, and strong correlations. These tools enable predictive calculations of optical and x-ray spectra and other excited state properties for a wide class of materials, and are widely used in research, e.g., at DOE synchrotron x-ray facilities. Besides x-ray absorption, a number of new spectroscopies are of interest. For example, RIXS (resonant inelastic x-ray scattering) makes possible simulations of high resolution spectroscopy measurements using x-ray scattering techniques, while calculations of the Compton profile are now important in characterizing the equation of state of warm dense matter.

FY 2012 HIGHLIGHTS

A major success has been the development of many-body techniques beyond the conventional GW quasi-particle approximation. Our approach is based on the cumulant expansion and the quasi-boson method. This research is of fundamental importance in understanding excited states in condensed matter. Our approach has recently been used to explain XPS measurements of condensed and molecular systems and has led to two Physical Review Letters. The first is a quantitative explanation of the multiple-plasmon satellite structure in the valence XPS of bulk Si. The second is a quantitative treatment of non-stoichiometric effects in the XPS of small gas phase molecules; this latter work was also chosen as a Synchrotron Soleil highlight in 2012. We have also succeeded in extending the theories used in our codes to include Hubbard model corrections and multiplet effects. These advances permit an approximate treatment of strong-correlation effects in many materials. Finally we have extended our codes to permit calculations of RIXS and the Compton profile, spectroscopies which are of substantial current interest.

Interplay between Superconductivity and Magnetism in Iron Based superconductors

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Funding:	$300,000

PROGRAM SCOPE

The goal of the project will be 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. My goal is 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. 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, spin-fluctuation approach leads to an attraction in both d-wave and extended s-wave (s+-) channels; and the type of order the system chooses at a given doping becomes an issue. 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 proposed study of the interplay between magnetic and superconductivity should have an impact on these systems as well.

FY 2012 HIGHLIGHTS

The project started on September 1, 2012. Thus far, we have successfully explained vertical line nodes observed in one class of FeSCs as being due to symmetry-allowed hybridization between electron pockets. Another project, which is near completion, is the theoretical prediction for completely novel s+is superconductivity in hole-doped Fe-pnictides. Such superconductivity breaks time-reversal symmetry and is highly desirable for applications.

Electron Coherence and Interactions in Nanostructures

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Funding:	$175,000

PROGRAM SCOPE

The program addresses kinetic phenomena in quantum wires, metallic rings, and loops made of small Josephson junctions. In the part devoted to quantum wires, we are developing kinetic theory for interacting electrons with a generic dispersion relation (the nonlinear Luttinger liquid). We apply this theory to explain the observed particle-hole asymmetry of electron relaxation in single-mode wires, and to predict electron relaxation rates in edge modes formed in a two-dimensional electron liquid by a quantizing magnetic field. In the metallic rings direction, we are interested in the nonlinear dc response to a microwave field of an array of nanorings; the aim is to elucidate the effect of microwave radiation on the persistent currents. In the part devoted to quantum kinetics of Josephson junctions arrays, we consider the effects of coherent phase slips; we aim at understanding the relaxation mechanisms of low-energy excited states in a loop of junctions. All parts of the program are related to ongoing experiments.

FY 2012 HIGHLIGHTS

Electron energy partition and relaxation in quantum wires. Fabrication of semiconductors-based parallel quantum wires facilitated the studies of momentum-resolved electron tunneling. Experiments in the group of Prof. Amir Yacoby (Harvard University) revealed a puzzle: the relaxation of charge carriers apparently was strongly dependent on the polarity of the bias which injects the carriers into the wire. That striking result found a natural explanation in our theory of the nonlinear Luttinger liquid. It predicts slow relaxation of holes and much faster relaxation of particles (having velocities higher than the density wave mode). We developed a detailed perturbative theory of the particle-hole asymmetry of the relaxation rates for spin-degenerate electrons in a single-mode quantum wire. The rate equations based on the evaluated rates explained quantitatively the observations.

DOE National Laboratories

Exploratory Development of Theoretical Methods

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Students:	2 Postdoctoral Fellow(s), 1 Graduate(s), 1 Undergraduate(s)
Funding:	$764,000

PROGRAM SCOPE

The purpose of this FWP is to generate new theories, models, and algorithms that will be beneficial to the research programs at 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.

FY 2012 HIGHLIGHTS

(1) Methods for crystal structure prediction and material discovery – We developed a fast and efficient adaptive genetic algorithm (GA) method for crystal structure prediction. This method combines the speed of empirical potential searches with the accuracy of first-principles calculations. The efficiency of the adaptive GA method allows a great increase in the size and complexity of systems that can be studied. The performance of adaptive GA is demonstrated by the predictions of several new high pressure phases for SiO_2, ice, and $MgSiO_3$. We also developed strong interactions with the magnetism groups at Ames Laboratory to describe and predict structures and properties of new magnetic materials.

(2) Methods for strongly correlated electron systems – We extended our Gutzwiller DFT approach to obtain new formulation for exchange-correlation energy and total energy functionals for strongly correlated electron systems. The Gutzwiller approximation is replaced by a correlation matrix renormalization (CMR) approach in which both the one-particle density matrix and the two-particle correlation matrix of the system are renormalized from the Hartree-Fock values according to local electron correlation effects. The method calculates the Coulomb integrals explicitly without assuming the screened Coulomb interaction parameters. There are also no double counting issues commonly encountered in previous many-body approaches.

(3) Methods for spin dynamics and quantum control of spin – We developed novel theoretical techniques for investigating and controlling the quantum spin dynamics of individual electronic and nuclear spins in solids. We demonstrated how our theoretical work helped understand the quantum dynamics of individual spin impurities in diamond, and guided joint theory/experiment work on controlling a single quantum spin in solid-state environment and implementing decoherence-protected controlled dynamics of two coupled spins. As a result, we were able to realize the first quantum computation (quantum search algorithm) on two individual solid-state spin qubits, and, using this advance, demonstrate extremely sensitive nanoscale tomography with single-spin resolution in solids.

Metamaterials

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Students:	4 Postdoctoral Fellow(s), 3 Graduate(s), 0 Undergraduate(s)
Funding:	$487,000

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 2012 HIGHLIGHTS

Bringing Gain to Metamaterials – Energy is lost by conversion of light to heat in the metallic constituents of metamaterials, in particular at optical wavelengths where losses are large. Thus, reducing or compensating losses is a key challenge for metamaterial technologies. It is of vital importance to understand the mechanism of the interaction between metamaterials and gain media. We demonstrated that the differential transmittance—transmittance with gain minus transmittance without gain—can be negative, a quite unexpected result. This behavior can be attributed to the strong coupling between the resonances of metamaterials and the gain medium. Our work provides a novel tool to select new metamaterial designs with optimally low losses.

Identifying Good Conductors for Metamaterials and Plasmonics – We identified the material parameters related to two limitations imposed on optical metamaterials: (1) dissipative loss in their metallic constituents and (2) the saturation of the resonance frequency. We found that the material parameter determining dissipative loss is the conductor's real part of the resistivity, and a critical structural parameter is the conductor's thickness. Using these considerations, we compared various conductors (metals, transparent conducting oxides, graphene, superconductors) and approaches for the design of high-quality optical metamaterials.

Dynamic and Tunable Metamaterials – Metamaterials that can provide a switchable or tunable response controlled by an external parameter are highly desirable for the development of advanced devices, especially in the terahertz frequency range. We developed optically switchable THz modulators capable of dual-band operation. These modulators consist of resonant metallic metamaterials fabricated on substrates with photo-excitable free charge carriers to modulate the metamaterial's response. We demonstrated giant optical activity and dynamic tunability of polarization modulation.

Nanoscale Magnetism

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Students:	4 Postdoctoral Fellow(s), 4 Graduate(s), 2 Undergraduate(s)
Funding:	$1,078,000

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 unusual magnetic materials to gain fundamental new knowledge, and also to exploit that knowledge. The program engages in basic research to discover new magnetic materials with unique, useful, and controllable/tunable properties.

FY 2012 HIGHLIGHTS

A highly visible breakthrough was analysis of spin dynamics at Nitrogen-Vacancy (NV) defects in diamond, allowing room temperature access of microwave magnetic field manipulation and interrogation of non-equilibrium quantum dynamics for single spins. Computational and theoretical analysis from Ames was instrumental in developing pulse sequencing for control and decoupling from the environment.

Another highlight was the theoretical prediction and experimental observation (magneto-optics) of unusual surface magnetism on cleaved samples of $BaMn_2As2$, a narrow gap antiferromagnet, with a Néel temperature of ~640K and ~3.8 μ_B moments on Mn. Analysis of the magnetic surface "domains" is ongoing.

Successful synthesis and modeling of polyoxometalate single-molecule magnets with large magnetic anisotropy was completed, and new magnetic molecule projects involving Ce_{13}, Pr_{13}, and Nd_{13} were begun. There is a developing overlap with the interests of the FWP of Surya Mallapragada where the aim is the synthesis of "nanostructures such as complex magnetic nanocrystals with potential energy relevance."

Controlled epitaxial growth of magnetic few atomic layer nano-islands (Gd,Dy,Fe,Eu) on graphene and W(110) was completed. Correlation of island morphology and magnetic properties, in situ with spin polarized STS and ex situ (under way with SMOKE and ultrafast optics after islands are capped) in collaboration with FWP "Surfaces far from equilibrium." Detailed study of the Gd(0001) surface state spin polarization as a function of growth conditions and island height.

Definitive new insights (and a PRL) on $LaCoO_3$ were obtained by analysis of x-ray absorption and magnetic dichroism experiments. This material's strange magnetic properties (also with doping) have been the subject of over 2,000 publications in the last 50 years.

Finally, we have worked with analyzing the influence of magnetism on the properties of the FeAs based superconducting materials; in particular, the local magnetic moments on Fe, which are disordered at room temperature, were found to be essential in calculations to obtain agreement with several branches of the phonon dispersion curves as measured by inelastic x-ray scattering.

Condensed Matter Theory

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Funding:	$1,600,000

PROGRAM SCOPE

Condensed matter theory research programs in MSD are currently carried out in the general areas of superconductivity, spectroscopy, and nanoscience, with an emphasis on interaction with various experimental programs within MSD. Our long-term goals are 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 oxides with novel properties, quantum phase transitions in strongly correlated electron systems, and transport in quantum wires, quantum dots, and spintronic devices. We are also developing as a major center for theoretical analysis of spectroscopic and transport 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 laboratory programs.

FY 2012 HIGHLIGHTS

In the correlated electron part of the program, we have achieved a fundamental understanding of the charge density wave state in $NbSe_2$, being able to model both ARPES and scanning tunneling spectra by assuming an energy gap whose center is displaced off the Fermi energy, indicating that the CDW state is not driven by nesting. We have also been able to derive detailed expressions for x-ray dichroism coming from toroidal dipoles and magnetic quadrupoles, and suggest that the observed dichroism signal in CuO is not a signature of this as the measurements were not done in the magnetoelectric phase. Finally, we have been able to show from both a Boltzmann and a Kubo treatment that the single particle and transport lifetimes are equivalent in the Kondo-Heisenberg model and can give rise to a novel linear in T resistivity as observed in experiment.

In the mesoscopics part of the program, we have developed a theory of the equilibration rate of a system with arbitrarily strong interactions between particles, valid for both fermions and bosons. We obtained a complete expression for the equilibration rate in terms of the spectrum of hole-like excitations in the system, which can be measured independently in experiments on tunneling between parallel wires. In a related project, we have studied the inelastic lifetime and equilibration of thermal excitations in a strongly interacting one-dimensional system described as a Wigner crystal, and also studied how this strongly interacting system thermalizes. We have been able to solve the linearized Boltzmann equation for the bosonic excitations *exactly* and determine the whole spectrum of the relaxation times and relaxation modes.

Materials Theory Institute

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Sr. Investigator(s):	
Students:	0 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$250,000

PROGRAM SCOPE

The central vision of the Materials Theory Institute (MTI) is 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: (1) promising new opportunities arising from MSD research and (2) new directions in condensed matter and materials science arising from the broader community. 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 a series of the topical workshops on the most urgent subjects related to existing MSD projects which promise to stimulate new research directions at MSD.

FY 2012 HIGHLIGHTS

(1) Workshop on Physics of Bacterial Communities, June 11-12, 2012, Notre Dame Chicago Commons, Chicago, IL. Organizers: Mark Alber, University of Notre Dame; Igor Aronson, ANL. The focus of the workshop was on the fundamental understanding of physical mechanisms governing microbial actions, including cellular responses to chemical and physical perturbations, interactions between cells, and temporal and spatial coordination of these events. The workshop brought together physicists, biologists, applied mathematicians, and computational scientists to discuss the latest developments in the physics of bacterial communities, including swarming, quorum sensing, cell signaling, and biofilm formation, and effects of bacterial activity on environment and health.

(2) MTI visit of Shi-Zeng Lin, Sep 30-Oct 13, 2012, hosted by Alexei Koshelev and Ulrich Welp: *Theoretical study of linewidth of the terahertz radiation from intrinsic Josephson junctions (IJJs) in high-T_c cuprate superconductors.* The terahertz (THz) radiation from the BSCCO high-T_c superconductor has attracted considerable interest during the last several years because this unique THz source is promising to fill the long-sought THz gap. One unsolved theoretical issue is the linewidth of radiation for this THz source, which has been measured experimentally very recently. In this project, we investigated the linewidth of the radiation from BSCCO single crystal both in the case of free-standing crystal and mesa structures. The equation of motion for the superconducting phase in the presence of in-plane and out-of-plane fluctuating quasiparticle currents was derived. It was found that the radiation into the substrate is the dominant dissipation and, thus, it is most important for the broadening of the radiation line.

Optimizing Superconductor Transport Properties through Large-Scale Simulation

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Funding:	$500,000

PROGRAM SCOPE

The main goal of this SciDAC partnership is the optimization of superconductors for energy applications using large-scale computations. Most energy applications of superconductivity, such as power transmission over superconducting cables, are based on achieving low energy dissipation in high-temperature superconductors. Dissipation is minimized by restricting the mobility of the vortices carrying magnetic field in the superconducting material by pinning them with admixed inclusions. Understanding the interaction of vortices with general configurations of inclusions is a major outstanding challenge both for fundamental science and energy applications. The task is complicated by the high density of the vortices, their mutual long-range interaction, and the dependence of their behavior on external parameters, such as temperature and the applied magnetic field. These features in general preclude an analytical description of vortex dynamics and, until recently, made numerical simulation prohibitively expensive. The new capabilities of DOE's leadership-class computing hardware and the development of scalable algorithms and software now put detailed numerical investigation of vortex pinning within reach. Capitalizing on these developments, this project aims to advance the fundamental understanding of vortex dynamics in superconductors and to determine the optimal size, shape, and concentration of the admixed particles required to achieve optimal power transmission properties.

Quantum Mesoscopic Materials and Structures

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Students:	1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$780,000

PROGRAM SCOPE

The central vision of the Quantum Mesoscopic Materials Program is to develop models and theories that will open possibilities for the design of new materials with desirable properties and controllable behavior. The strategy of the program is based on creation of nanoscale metamaterials, such as granular structures, Josephson arrays, and low-dimensional nanopatterned structures. Deriving from the accomplishments of the first three years, we define our strategic priorities as (1) comprehensive formulation of a theory of superconductor-to-insulator including a consideration of the superconductor-superinsulator transition, the role of Coulomb effects, and quantum and thermal fluctuations; (2) a general comprehensive theory of far and very far from equilibrium processes and its applications to transport in non-standard insulators including tunneling processes, nonlinear behaviors, and memory effects; (3) thermal transport and thermoelectric effects, and electronic transport and heating 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 transport in disordered films and SNS structures; and (5) condensation and localization of polaritons in crystals and metamaterials.

FY 2012 HIGHLIGHTS

(1) Stimulation of the Fluctuation Superconductivity by PT Symmetry: A Hermitian character of the Hamiltonian ensuring that the energies of its stationary states are real is a cornerstone of quantum mechanics. It was recently discovered that the weaker requirement of combined parity reflection and time reversal introduces new classes of Hamiltonians whose spectra are still real and positive. This generalization of Hermiticity opened a new field of research in quantum mechanics that has been ever since enjoying rapid growth. We discuss fluctuations near the second-order phase transition where the free energy has an additional non-Hermitian term. The spectrum of the fluctuations changes when the applied field exceeds the critical value corresponding to the PT-symmetry breakdown of the effective non-Hermitian Hamiltonian. We calculated fluctuation contributions to the differential resistance of a superconducting weak link and found the manifestation of the PT-symmetry breaking in its temperature evolution. We validated our theory via measurements in mesoscale-patterned superconducting wires.

(2) Superconducting Phase Transitions In Ultrathin TiN Films: Calculating quantum contributions to conductivity, we demonstrated that the resistance of thin superconducting films is non-monotonic in temperature due to the competition between weak localization, electron-electron interaction, and superconducting fluctuations. We showed that superconducting fluctuations give rise to an appreciable decrease in the resistance even at temperatures well exceeding the superconducting transition temperature.

Robust Electronic Structure Methods for Defect and Interface States in Oxide Heterostructures

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von Lilienfeld, Anatole, Argonne National Laboratory
Students: 2 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding: $308,000

PROGRAM SCOPE

The focus of this proposal is to understand and tailor quantitative models of correlation physics in accurately parameterized model Hamiltonians. This project will use ab initio methods to define reduced basis sets which adequately capture the physics of a set of target physical systems where many-body correlations are important. Given these accurately parameterized models, we will then develop dynamical-mean-field-theory codes, as well as other methods, for the solution of basic problems involving the determination of band offsets, defect energetics, impurity band physics, and excitonic states. We will make available “solvers” for these problems to the community, aiming in particular to provide codes useful to experimentalists as they analyze their data, and will port the methods where appropriate onto high performance computers. The science agenda that frames our methodology is that of atomically controlled oxide heterostructures. This topic has the potential to combine the atomistic control of semiconductor physics with the richness of the physical phenomena seen in correlated oxides. Experimental progress in such well-controlled systems will be used to provide sharp validation of theory.

Condensed Mattery Theory

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Sr. Investigator(s): Konik, Robert, Brookhaven National Laboratory
Ku, Wei, Brookhaven National Laboratory
Students: 1 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding: $1,450,000

PROGRAM SCOPE

The goal of the program is to study systems with strong correlations. In condensed matter physics, such correlations usually originate either from strong lattice interactions (e.g., strong local Coulomb repulsion in narrow band systems) or, in low dimensional systems, strong quantum fluctuations. Examples of strongly correlated systems include heavy fermion materials, quantum magnets (especially frustrated ones), so called bad metals, cuprate and iron-based superconductors, quasi-one-dimensional materials, quantum dots, and many others. The strength of correlations makes the conventional computational methods ineffective and requires special analytic and numerical approaches. We use a combination of analytical methods, such as bosonization and theory of integrability, and new numerical tools developed in our group by R. M. Konik. In this method, the Hamiltonian of any given system is represented as a sum of an integrable part and a perturbation. One takes advantage of the fact that the eigenfunctions of the integrable part are known explicitly and hence matrix elements of the perturbation can be calculated analytically. The numerical procedure is then used is to diagonalize big matrices consisting of the bare Hamiltonian and the perturbation.

FY 2012 HIGHLIGHTS

(1) We have suggested a microscopic mechanism of finite wave number superconducting pairing which does not require a magnetic field. We suggest it as a mechanism for exotic two-dimensional superconductivity in LaBaCuO, recently discovered by Tranquada's group at Brookhaven National Laboratory. [Physical Review B 85, 195103 (2012)]

(2) Using a numerical renormalization group based on exploiting an underlying exactly solvable non-relativistic theory, we study the out-of-equilibrium dynamics of a 1D Bose gas (as described by the Lieb-Liniger model) released from a parabolic trap. Our method allows us to track the postquench dynamics of the gas all the way to infinite time. We also exhibit a general construction, applicable to all integrable models, of the thermodynamic ensemble that has been suggested to govern these dynamics, the generalized Gibbs ensemble. We compare the predictions of equilibration from this ensemble against the long-time dynamics observed using our method. [Physical Review Letters 109, 175301 (2012)]

Electronic Properties of Transition-Metal-Compound Nanotubes

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Sr. Investigator(s):	Yin, Weiguo, Brookhaven National Laboratory
Students:	0 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding:	$410,000

PROGRAM SCOPE

This program is directed on first-principles theoretical studies of electronic structure and excitation of several classes of transition-metal-compound nanotubes, and pronounced nano-scale physics in strongly correlated bulk materials. Beside the conventional first-principles methods, the study also includes new theoretical development to properly account for the strong many-body interactions and short-range order essential to the rich correlated nature of these materials. The goal of this research is to bring the scientific research field closer toward a broader and deeper understanding of electron correlations in these materials, thus guiding the discovery and design of new functional nanomaterials, especially for applications in solar energy, thermoelectricity, and superconductivity, all of which are essential to the central missions of DOE-BES and BNL. Specifically, in the past few years, special attention has been paid to the fundamental issues of Fe-based high-temperature superconductors and realistic effects of disorders in energy-application related functional materials. These efforts respond to the activities at BNL's Center for Functional Nanomaterials and the National Synchrotron Light Source.

FY 2012 HIGHLIGHTS

Three directions of researches were carried out: (1) physical effects of disordered impurities in Fe-based superconductors, (2) rich magnetic structure of Fe-based superconductors, and (3) systems with strong spin-orbit coupling. Particularly, the investigations of disordered Co/Zn substitution of Fe in Fe-based superconductors resolved the current debate on whether such substitution introduces additional carriers in the systems. The study of Fe vacancies in the Fe selenides revealed novel "effective doping" and existence of a large amount of diffusive hole carriers. Similarly, investigation of isovalent Ru substitution of Fe in Fe-based superconductors demonstrated the first realization of supperdiffusive carriers in real materials and explains the resilience of transport and superconductivity of this material. Finally, our study reveals the essential role of the lack of one-Fe translational symmetry of Fe-based superconductors in creating the widely discussed electron pockets.

The Materials Project Center for Functional Electronic Materials Design

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	Ceder, Gerbrand, Massachusetts Institute of Technology
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	Haranczyk, Maciej, Lawrence Berkeley National Laboratory
	Gunter, Daniel, Lawrence Berkeley National Laboratory
	Asta, Mark, California-Berkeley, University of
	Gamst, Anthony, California-Riverside, University of
Students:	6 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$3,000,000

PROGRAM SCOPE

Materials discovery and development is a key innovation driver for new technologies and markets, and an essential part of the drive to a renewable energy future. The goal of the Materials Project (online at http://www.materialsproject.org) is to accelerate materials discovery and education through advanced scientific computing and innovative design tools. The proposed work will significantly impact the scientific community, computer science research, and education by providing unprecedented data and materials design tools as well as comprehensive capabilities for scientists to share their processes and results. High-throughput calculations, state-of-the-art electronic structure methods, as well as novel datamining algorithms for surface, defect, electronic, and finite temperature property predictions will be combined with existing capabilities at the Materials Project for tens of thousands of materials to yield an unparalleled materials design environment. We envision a fundamentally networked and data-intensive model of scientific discovery where computation and simulation can be leveraged at a massive scale, where many of the mundane details of recording and saving work are handled by online services, where results can be immediately validated against high order methodologies and experimental results, and where the process of scientific discovery can leverage the accumulated knowledge of Nature with something akin to a Google search – "find the electrochemical properties and crystal structure for compound X."

FY 2012 HIGHLIGHTS

The Materials Project Center for Functional Electronic Materials Design was funded in August 2012 and is currently ramping up the effort according to the proposal plan. Good initial progress towards milestones has been made in terms of equipment, personnel, and scientific goals.

The $1 M cluster arrived late November and is being setup and configured at NERSC to accommodate the diverse materials calculations (DFT, GW, QMC, etc.) planned by the Center effort. Two postdocs have already joined the team, and three more will be coming onboard as of early January. The high-throughput infrastructure for surface calculations is being coded into the Materials Project code base. Automatic cleaving, equivalent k-point generation, and handling of absorbent species from water and air are in progress. The first step towards prediction of aqueous dissolution and precipitation has been made insomuch that the generation of element Pourbaix maps with calculated bulk data [see Persson et al, Phys. Rev. B 85, 235438 (2012)] compassing the entire MP database has been coded and is currently being tested. High-throughput standard DFT band structures are running on the Materials Project allocation at NERSC. Improved DOS handling, electronic effective mass calculations, Seeback coefficients, etc. are being implemented into the analysis Pymatgen code base. User commenting (crowd sourcing) is available online since October 2012.

Theory of Materials Program

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Sr. Investigator(s):	Cohen, Marvin, Lawrence Berkeley National Laboratory Lee, Dung Hai, Lawrence Berkeley National Laboratory Neaton, Jeffrey, Lawrence Berkeley National Laboratory Wang, Lin-Wang, Lawrence Berkeley National Laboratory
Students:	1 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding:	$759,000

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 are 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 2012 HIGHLIGHTS

We have performed ab initio studies of topological insulators, leading to an accurate description of surface-state dispersion and spin texture and to the possibility of controlling the spin polarization associated with a charge current in thin films by means of an external electric field. We have explored the electronic and optical properties of pure and modified Si and novel phases of Si for photovoltaics. We discovered a new phenomenon in magneto-optical response of graphene that involves resonant transitions of absorption of a photon together with the simultaneous creation of an intervalley, intra-Landau level exciton and a K-phonon.

We have studied quantum spin Hall insulator in the presence of Hubbard U using field theory, yielding results on edge modes, low-energy excitations, and phase diagram. We explored topological insulators on a Mobius strip, showing that while the flow pattern of edge currents can detect the twist of the Mobius strip in the case of Chern insulator, it cannot do so for spin Hall insulator. We also presented a theory of a 3D fractionalized topological insulator in the form of a U(1) spin liquid with gapped fermionic spinons in the bulk and topologically protected gapless spinon surface states.

We have released a public domain suite of codes, the BerkeleyGW package, for state-of-the-art computation of excited-state (spectroscopic) properties based on the GW/GW-BSE approach, the first such U.S. public domain package. We continue to improve (through new formulations and methodology developments) methods for *ab initio* calculations of ground- and excited-state properties of materials.

Discontinuous Methods for Accurate, Massively Parallel Quantum Molecular Dynamics: Lithium Ion Interface Dynamics from First Principles

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Students:	2 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$189,000

PROGRAM SCOPE

The goals of this project are to develop and employ, for the first time, modern Discontinuous Galerkin (DG) techniques to accomplish quantum molecular dynamics (QMD) on an unprecedented scale; and to apply the new methodology 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, for a subset of systems within their reach (< 1000 atoms) while the new DG methodology is developed and verified. We then apply the new DG methodology 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 new DG method achieves planewave accuracy in both total energy and forces with a few tens of basis functions per atom. The basis is strictly local and systematically improvable, thus enabling high accuracy and efficient large-scale parallel implementation. By virtue of these properties, the initial implementation has already accomplished *ab initio* calculations with over 3,000 atoms with planewave accuracy. These key properties are made possible by releasing the constraint of continuity in the representation through the DG formulation of the Kohn-Sham equations. To reach the largest system sizes, a new Fermi Operator Expansion formulation (PEXSI) will be employed, eliminating the need for diagonalization while retaining strict systematic improvability and applicability to both metals and insulators, above room temperature and below. In partnership with the SciDAC FASTMath Institute, a massively parallel implementation will be developed, parallelizing over *k*-points, expansion poles, elements (subdomains), and within elements, to scale efficiently to in excess of 100,000 processors on current and next generation leadership-class supercomputers. Upon completion, the resulting method and code infrastructure will be made available to the broader research community to accelerate progress in the gamut of applications areas susceptible to such large-scale *ab initio* modeling.

Accelerated Molecular Dynamics Methods

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Sr. Investigator(s):	Danny, Perez, Los Alamos National Laboratory
Students:	2 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$460,000

PROGRAM SCOPE

The goal of this project is to develop high-quality computational methods for reaching long time scales in atomistic simulation of materials. While direct molecular dynamics (MD) is limited to roughly one microsecond, it is often crucial to probe longer time scales. We focus on infrequent-events, as this characterizes the long-time dynamics of nearly every material process of importance to LANL and DOE missions. For this type of system, we can shorten the time between successive events that take the system from state to state. Largely under this BES program, we developed the accelerated molecular dynamics (AMD) methodology, in which we let the system trajectory itself find an appropriate way out of each state. With three AMD methods in place, our main focus now is on making them more powerful and efficient for a wide variety of realistic systems, fully exploiting upcoming computer architectures, and making the methods available and effective for materials experts.

FY 2012 HIGHLIGHTS

This year, we completed two important generalizations of existing AMD methods. First, we developed a local version of hyperdynamics. Standard hyperdynamics is limited to rather small systems because a requirement in the method is that there cannot be any time acceleration when the system is near to making a transition, something that happens frequently for larger systems. The new hyperdynamics is reformulated to exploit the fact that most transitions are local in nature. We have demonstrated its accuracy and have shown that it can scale to arbitrarily large systems. Second, we derived a solid formal understanding of the parallel-replica dynamics method in its full generality, where the states of the system are defined by arbitrary volumes in configuration space. We demonstrated that, despite this fully general choice, parallel-replica dynamics remain arbitrarily accurate, but their efficiency will be dictated by the particular nature of the states. This flexibility can be exploited to tailor the states to the system at hand, allowing us to accelerate the dynamics of much more complex systems than ever before.

We applied AMD techniques to a variety of problems of technological importance, including grain-boundary-assisted healing of radiation damage in metals, transformation of nanotube fragments into graphene, and dynamics of interstitial clusters in Zr. We also pursued our investigation of nanoscale friction by revisiting a widely used theoretical rate-theory model. Finally, we also investigated the synchronization behavior of Langevin thermostats (the tendency of different trajectories to merge when exposed to the same noise) when there is local disruption of the dynamics. We demonstrated that, in three dimensions, a local disturbance only locally disrupts synchronization, a property we can exploit to increase the effectiveness of the AMD methods.

Integrated Modeling of Novel Materials

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Students:	2 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$380,000

PROGRAM SCOPE

Inhomogeneity in real and momentum space is a key ingredient that controls the functionality of materials. We develop the theoretical tools and methods that are necessary to model the spatially inhomogeneous competing states of correlated materials. Our approach calls for a set of combined techniques that make contact with the momentum space characterization of nonuniform materials.

Our approach is inherently multiscale. It connects the effective models of competing interactions with nanoscale modulations and first-principles approaches with real space dependent parameters in an effort of new transport and thermodynamic macroscale modeling. This integration adds an important verification, validation, and prediction tool to materials modeling.

FY 2012 HIGHLIGHTS

(1) We made tremendous progress in the development of many-electron methods integrated with first-principles approaches for dynamic correlation effects in actinide materials. We demonstrated the connection between spin fluctuations and the peak-dip-hump feature in photoemission spectra of several actinide compounds. In addition, we validated the prediction of electronic hot spots in these spectra by the analysis of angle-resolved photoemission experiments. Better understanding of strong electron interactions in correlated materials and identifying electronic hot spots in momentum space may provide the basis for tuning and predicting improved functionality in old and new materials. [Das et al., Phys. Rev. Lett. 108 (2012) 017001; Das et al., Phys. Rev. X (in press)].

(2) We modeled the quasiparticle interference (QPI) pattern in recently discovered iron-based high-temperature superconductors. Our calculations showed that in the superconducting state, due to the absence of hole pockets at the Brillouin zone center, the quasiparticle scattering occurs between electron pockets at the zone boundary. We predicted that significant contrast in the QPI pattern between the superconducting d-wave and isotropic s-wave pairing states can be used to probe the pairing symmetry within the Fourier-transform scanning tunneling microscope (STM) technique. [Zhu and Bishop, Europhys. Lett. 100 (2012) 37004].

Extending the Reach of Computational-Theoretical Methods to Materials at the Energy Frontier

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Students:	0 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$1,397,000

PROGRAM SCOPE

This program is designed to significantly improve our description and understanding of electronic correlations, magnetic interactions, and spin-orbit coupling in an *ab initio* framework. This advance is key for the design of new materials for clean energy. Our goal is to describe the physical, chemical, and electronic properties of materials with accuracy comparable to experimental characterization and in large physically-relevant systems. This program includes both accurate *ab initio* approaches and methods based on simpler models. Models will allow us to test new methods and extend *ab initio* results to larger systems. A priority is to develop, improve, and implement in high-performance supercomputers new theories that go well beyond the current approaches. Accordingly, we aim to provide an alternative route using the highly-accurate Quantum Monte Carlo (QMC) and/or improved DFT approximations. The results provided by our research will quantify the errors of the widely used DFT approximations. When even higher performance/high-capacity computers become readily available to a larger group of researchers, we aim to provide an alternative QMC-based approach to reach the required accuracy for energy applications.

FY 2012 HIGHLIGHTS

A complete extension of the diffusion Monte Carlo (DMC) algorithm using complex valued wave functions as guiding trial wave functions has been applied to the self-healing DMC (SHDMC) method and validated with model calculations. Thus, SHDMC could allow the calculation of systems with current or applied magnetic fields. Newly developed fast algorithms to evaluate multi-determinants and improved optimization methods in QMC have been applied to benchmark binding energies of first row dimers and the 55 molecules of the G1 test set. This study demonstrated the potential recipe to systematically reduce the fixed-node error in QMC. In collaboration with Kent and Ganesh from ORNL CNMS, Kim and Reboredo have obtained 45 million core hours to perform QMC calculations on Titan.

First-principles evaluation of the partition function that determines thermodynamic properties are reported in two published papers: one on the *convergence for the Wang-Landau density of states* and the other on *perturbation calculation of thermodynamic density of states*. The transfer of first principles energies to model Hamiltonians has allowed us to treat Fe with full coupling of vibrational and spin degrees of freedom. Our WL-LSMS code has been ported (with ASCR support) to take advantage of GPU based accelerator and has been shown to achieve a performance of 746 GFLOP/s per node on the new Titan computer at Oak Ridge and to scale to the full machine. Eisenbach, Nicholson, and Stocks have been awarded 105 million core hours through an INCITE project.

Materials Theory

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Du, Mao-Hua, Oak Ridge National Laboratory
Fu, Chong Long, Oak Ridge National Laboratory
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Funding: $1,392,000

PROGRAM SCOPE

Theory plays an important role in condensed matter and materials science efforts by interpreting experiments, defining critical measurements, identifying novel phenomena and materials in which they are realized, and providing understanding of the diversity of matter and materials properties. This project pushes forward at the frontiers of condensed matter and materials science, using state-of-the-art materials and specific theoretical tools to develop understanding of materials properties. Working in conjunction with ORNL and external experimental efforts, we will unravel the chemical and structural underpinnings of collective properties in specific materials, develop understanding of novel phenomena and materials, and devise new compounds with novel and useful properties. The essential aspect is the use of methods that directly incorporate the chemical make-up and detailed structure of materials and thereby enable direct connections with experiments. A key to success of this effort will be exploitation of natural synergies between theory and experiment. Impacts include microscopic understanding of materials properties, such as ferroelectricity, magnetism, new concepts for functional hetero-structures, and the elucidation of chemical and physical trends leading to the discovery of new advanced materials. The main scientific thrust is the exploration of the key physical phenomena in advanced functional materials, including magnetic materials, ferroelectrics, energy storage interfaces, and materials with unusual characteristics, such as uncommon bonding patterns. The long-range goal is to provide understanding and elucidate trends that point the way to new materials for energy applications.

FY 2012 HIGHLIGHTS

Our focus this year has been on understanding materials behavior and using this to interpret experiments and predict new materials. The work has included studies of ferroelectric, magnetic, superconducting, dielectric, and optical materials, examples of which follow. We elucidated a mechanism for reducing band gaps of ferroelectrics by site-specific substitution combined with oxygen vacancies. We explained how to improve electron mobilities at oxide interfaces by fractional delta doping. We studied the crystallographic structure of perovskite $Bi(Mg,Ti)O_3$, showing it to be a lead free analogue of $PbZrO_3$. We showed that delafossite structure $PdCrO_2$ is a three-dimensional itinerant magnetic system. We used first principles calculations to demonstrate that marcasite $CrSb_2$ has quasi-one-dimensional magnon dispersions with implications for transport. We found that nitrogen impurities in zirconia form an unusual strongly bonded state associated with the formation of nitrosyl units—a finding of importance in understanding the effect of nitrogen on the stability of zircaloy corrosion barriers. We studied and explained the optical and transport properties of novel zintl phases including $BaCu_2Te_2$ and $BaCu_2Se_2$. Finally, we demonstrated that the role of hydration in sodium cobaltate is to induce ferromagnetic fluctuations, implying that the superconductivity of the hydrated compound is of triplet symmetry.

Network for Ab Initio Many-Body Methods: Development, Education and Training

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Sr. Investigator(s):	Morales, Miguel, Larence Livermore National Laboratory Greeley, Jeff, Argonne National Laboratory Shulenberger, Luke, Sandia National Laboratory Ceperley, David, University of Illinois
Students:	0 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$882,000 (combined funding for all institutions)

PROGRAM SCOPE

For many classes of materials and molecular systems, existing theoretical methods based on quantum mechanics offer a predictive capability: properties and performance can to a meaningful accuracy be calculated without empirical tuning parameters. The importance of a predictive capability cannot be overstated; it is the very foundation of viable efforts in computational materials design. For other classes of materials, as well as combinations of solid and molecular systems, a predictive capability is still lacking, a major hindrance to rapid progress.

The continuum quantum Monte Carlo (QMC) method, however, uniquely offers a path towards high accuracy calculations for a broad range of electronic systems. Localization, van der Waals interactions, and strong correlations between electrons can all be treated with high fidelity. Recent advances in QMC methods, algorithms, and codes have notably expanded the use of QMC. This proposal brings developers of electronic structure methods together to build a QMC framework supporting continuing theoretical development and providing rapid paths towards broader 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, and high-pressure materials. Our work will provide direct answers to fundamental materials science questions in these problems and establish benchmark levels of accuracy that will, in turn, provide targets for future developments in other electronic structure approaches.

The funding shown is for all institutions.

FY 2012 HIGHLIGHTS

We have initiated QMC study in catalysis and bulk properties, including testing of new approaches to generate pseudopotentials optimized for QMC and benchmark calculations of bulk Ar, Pt, and Au. To facilitate interactions, a collaborative wiki and code and data repositories were established. During the early science access periods at Oak Ridge and Argonne Leadership Computing Facilities, we have successfully ported QMCPACK on the new platforms and started the proposed development work on these systems.

Theoretical Studies of Collective Phenomena

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Students:	0 Postdoctoral Fellow(s), 3 Graduate(s), 0 Undergraduate(s)
Funding:	$1,369,000

PROGRAM SCOPE

This proposal describes a theoretical effort to study the emergence of complex collective electronic states in several families of materials, such as high temperature superconductors, ferrites, cobaltites, molecule-based magnets, multiferroics, and a variety of artificially-created superlattices and interfaces involving oxide perovskites. These compounds have several simultaneously active degrees of freedom, forming complex states where the competing tendencies are delicately balanced. Our 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. The specific proposed work has three 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. 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 2012 HIGHLIGHTS

Okamoto predicted novel quantum Hall effects in the artificial heterostructures of perovskite transition-metal oxides grown along the [111] crystallographic axis. In particular, Au-based oxide heterostructures are predicted to become quantum spin-Hall insulators at room temperature [Nat. Commun. 2:596 doi: 10.1038/ncomms1602 (2011)].

With members of the Neutrons Sciences Division, Fishman used the low-energy spin-wave spectrum to predict the single–ion anisotropy and Dzyaloshinskii-Moriya interaction in the important room-temperature multiferroic material $BiFeO_3$ [Phys. Rev. Lett. 109, 067205 (2012)]. Understanding the microscopic interactions of this material will allow it to be used in memory storage and spintronic applications. Fishman also studied the effect of quantum spin fluctuations on the distorted helical states of multiferroic materials [Phys. Rev. B 85, 024411 (2012)].

Moreo, Dagotto, and coworkers, including Alvarez from the CNMS, studied the transport anisotropy of spin-fermion models for the undoped limit of the iron-based superconductors via Monte Carlo simulations. The correct anisotropy found in experiments was reproduced. Fermi surface orbital order was found to be responsible for the anisotropy [Phys. Rev. Lett. 109, 047001 (2012)]. Dagotto and collaborators also studied exchange bias effects at the $SrRuO_3$/$SrMnO_3$ interface [Phys. Rev. B 84, 224437 (2011)].

X-ray Scattering

Institutions Receiving Grants

Multifunctional Materials Research using Ultrafast Optical Spectroscopy

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Students:	0 Postdoctoral Fellow(s), 2 Graduate(s), 1 Undergraduate(s)
Funding:	$194,000

PROGRAM SCOPE

The multifunctional properties of complex materials arise from subtle interplay between competing degrees of freedom. The results are dramatic and include, as examples, superconductivity and metal-insulator transitions. Associated with this diversity of phenomena is sensitivity to external stimuli enabling tuning of emergent macroscopic properties. Optical spectroscopy plays an important role in characterizing emergent properties with dynamic investigations playing an increasingly important role. We have a strong interest in using transient strain and transient electric fields to tune, drive, and control the macroscopic properties of complex materials. The goal of these studies is to investigate nonequilibrium phenomena in materials with strongly coupled charge, orbital, lattice, and spin interactions to access new macroscopic states. Specifically, we are using state-of-the-art optical techniques to generate high-field terahertz pulses to interrogate and control transition metal oxides. Our efforts focus on quantum dynamics associated with the insulator-to-metal transition in materials of contemporary interest that include vanadates, nickelates, and manganites. We are integrating metamaterials with these compounds to extend our experimental capabilities with a view towards creating new multifunctional materials and devices of relevance to DOE-BES.

FY 2012 HIGHLIGHTS

We have demonstrated driving the metal insulator transition in vanadium dioxide using picosecond electric field pulses. More generally, we have developed a powerful metamaterial-based platform to investigate low-energy dynamics in condensed matter and have shown that integration of metamaterials with complex matter is a viable pathway to realize functional nonlinear electromagnetic composites.

Real-Time X-Ray Studies of Surface and Thin-Film Growth Processes

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Principal Investigator: Karl, Ludwig
Sr. Investigator(s):
Students: 1 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding: $116,000

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. To develop these opportunities, we are utilizing a dedicated facility for real-time studies of surface and thin film processes at National Synchrotron Light Source beamline X21. We have been using the facility both to investigate fundamental growth issues in model systems and to examine kinetics in the technologically important cases of group III-nitride growth by molecular beam epitaxy and growth of dielectric and catalytic films by atomic layer deposition.

FY 2012 HIGHLIGHTS

We have collected data to compare and contrast the fundamental growth kinetics of sputter deposition and sublimation using a-Si as a model system. The kinetic energy of adatoms in the sputter deposition process appears to provide sufficient initial mobility for islands to form, grow, and coalesce. In contrast, during thermal deposition the surface immediately undergoes kinetic roughening. We have also investigated the kinetics of In and In-Ga droplet formation, growth, and coalescence, an important issue for group-III nitride thin film growth.

Nanoscale X-Ray Imaging and Dynamics of Electronic and Magnetic Materials

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Sr. Investigator(s):
Students: 1 Postdoctoral Fellow(s), 2 Graduate(s), 2 Undergraduate(s)
Funding: $185,000

PROGRAM SCOPE

A distinguishing attribute of correlated electronic and magnetic systems is that spin, orbital, and lattice coupling all have similar energy scales. These strongly competing degrees of freedom result in a wide variety of electronic and magnetic phases, with properties of materials easily tunable by temperature, chemical doping, magnetic or electric fields, strain, pressure, light illumination, and other parameters. At least in part, the complexity of the correlated electronic materials is due to the fact that these materials exhibit both intrinsic and extrinsic phase separation on diverse length scales, from nanometers to microns. The latter presents a significant roadblock towards unraveling the intrinsic physics because some of the most useful techniques in condensed matter physics lack the spatial resolution needed to explore phase transition phenomena at the relevant length scales.

We developed several new approaches to investigations of nanoscale structure and dynamics in a variety of electronic and magnetic systems using a suite of complementary synchrotron-generated x-ray scattering and imaging techniques.

FY 2012 HIGHLIGHTS

We have developed several new research directions, including new coherent diffractive imaging techniques based on x-ray ptychography. We have successfully performed to our knowledge first-ever coherent x-ray diffractive imaging (CXDI) of magnetic nanostructures, published last year in Proc. Of National Academy of Sciences in late 2011. We have also made several important developments in CXDI techniques and have applied them to both stand-alone, isolated nanostructures (nanowires, nano-islands) and extended objects, such as magnetic thin films (GdFe, FeRh). We have also successfully investigated a number of systems using scanning micro- or nano-diffraction (VO_2, Chromium, 1T-$TaSe_2$) and x-ray photon correlation spectroscopy. Many of these results have been published in *Applied Physics Letters* and *Nanoletters*, as well as *Physical Review* in 2012.

HPCAT -- An Integrated High-Pressure Facility at the Advanced Photon Source

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Funding:	$1,087,000

PROGRAM SCOPE

HPCAT's main goal is to provide a state-of-the-art user facility for advancing fundamental knowledge of materials behavior in a broad range of environments, such as pressure, temperature, radiation, and deviatoric stress, including both static and dynamic phenomena. 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, and (3) in situ measurements with high spatial resolution (1-3 microns) and high temporal resolution (down to 100 ps). Investigations of structure, equations of state, and electronic and magnetic properties provide critical data for code validation and tests of fundamental theory. The measured "structure-property" correlation helps to establish predictive models for developments of new materials and new applications. HPCAT has continued to stay at the leading position in the world, and is the most productive sector at APS in terms of the number of publications in "high-impact" journals as well as the total number of publications. In the past year, we have successfully commissioned the newly installed canted undulator and associated beamline optics, including two new monochromators, and made them fully operational to general users; we have enabled two new high-pressure x-ray techniques and further enhanced the three developed high-pressure x-ray techniques; and we have expanded supporting equipment critical for high pressure research.

FY 2012 HIGHLIGHTS

(1) We have successfully installed canted undulators in the fall of 2011. The canted operation has enhanced our facility, allowed for new capabilities to be developed, and increased the user activities. (2) By using x-ray focusing optics (x-ray capillary), we have successfully minimized the unwanted signals from walls of high pressure device in high pressure inelastic x-ray scattering measurements. (3) The in-line laser heating system has been significantly improved for studying matters under extreme conditions in a time resolved manner. (4) We have developed x-ray techniques for a comprehensive approach to study liquids at high pressures.

Magnetic and Superconducting Materials at High Pressures

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Funding:	$155,000

PROGRAM SCOPE

As a result of recent advances, experiments utilizing an unprecedented number of probes are now straightforward to perform over a wide range of pressures. This is especially important for testing theory; for example, a fundamental understanding of the mechanisms of superconductivity requires knowledge of crystal structure, electronic structure, and vibrational properties, including the interaction of the conduction electrons with lattice vibrations. Thus, our future studies will be centered around magnetic and transport measurements and complemented by a wide variety of high-pressure structural and spectroscopic methods involving laser and synchrotron radiation. The experimental challenges are:

(1) exploring new potential elemental superconductors (hydrogen) and already known superconductords (boron, sulfur, alkali metals, etc.) at the limit of static high pressure techniques;

(2) investigating special classes of superconducting compounds (hydrides; high-Tc superconductors, cuprates and Fe-based superconductors; borides, polyaromatic hydrocarbon superconductors) that may provide new fundamental knowledge and may prove important for application as high-temperature/high-critical parameter superconductors;

(3) investigating the pressure dependence of superconductivity and magnetic/phase transformations in 3d transition metal compounds including transitions from magnetic to nonmagnetic phases in a broad pressure-temperature range; and

(4) advancing transport and magnetic techniques for measurements on small samples at very high pressures in a wide temperature range, with the application of focused ion beam (FIB) technology tailored to the design of microcircuits down to a nanoscale size, thus expanding the horizon in the search for novel physical phenomena at ultrahigh pressures.

We will use the suit of transport techniques to measure the onset of superconducting T_c as a function of pressure in the multimegabar range, focusing on the superconductivity in hydrogen, and other simple elements at the limit of static high pressure techniques. The technique is based on a mutual induction principle involving micro-coils placed around the diamonds in a BeCu cell. This technique will be enhanced by the emerging microcircuit design aided by FIB or photolithography sample preparation, and will be extended with magnetic measurements by optically detected magnetic resonance from NV centers in diamond. We are implementing miniature diamond anvil cells suitable for superconductivity studies in various environments, including PPMS. Complimentary x-ray RIXS and other spectroscopic measurements of valence and core level excitations will be performed to probe the electronic structure and local spin state of 3d-metal ions. These new experiments have been made possible by the use of new Be gaskets and synchrotron x-ray methods. Raman scattering and synchrotron infrared techniques that we have developed will be used to study optical conductivity, magnon and phonon excitations, and phase transitions. A suite of x-ray diffraction techniques will be used for structural studies of single-crystal and polycrystalline samples.

Quantifying Damage Accumulation during Ductile Plastic Deformation using Synchrotron Radiation

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

PROGRAM SCOPE

This project uses a combination of recently developed experimental techniques at Advanced Photon Source beamline 1-ID to observe the process of damage accumulation in metals as they undergo tensile deformation. Observed responses of microstructures at the meso-scale include non-uniform lattice rotations, defect accumulation and migration, and slip along preferred crystallographic directions. All of these processes depend on the polycrystalline environment of each grain. At high deformation, voids form and coalesce causing failure of the material. Gaining a quantitative understanding of all of these response mechanisms has been difficult due to the lack of experimental probes that can directly observe them in three dimensions. Our near-field High Energy X-ray Diffraction Microscopy measurements track lattice orientations over cubic millimeter sized volumes with micron scale position resolution. High energy absorption tomography is performed on the same samples leading in principle to the ability to correlate void formation with microstructural features such as grain boundaries, triple lines, or quadruple points. The impact of the measurements is extended through computational modeling using the measured microstructures as input. A relatively new Fast Fourier Transform-based method is used that permits the viscoplastic stress-strain response of polycrystals to be calculated from a direct image of the microstructure. This type of comprehensive study of a small number of model systems (thus far, copper and zinc) should yield validated and predictive microscopic computational models for processes that have previously been understood only in a statistical sense. Lessons learned from these initial studies should allow generalizations to other systems. The methodologies and experimental capabilities developed within the project will be directly generalizable to other materials and processes of practical interest.

FY 2012 HIGHLIGHTS

High energy synchrotron x-rays were used to non-destructively map crystal orientations in copper and zirconium polycrystals as the samples were deformed. In zirconium, we have observed twinning transformations in a small number of grains whose orientations made them particularly susceptible. Model calculations are being used to test the extent to which the specific nucleation locations and geometries can be predicted by current models. In copper, we have observed the anisotropic development of lattice defects in the early stages of deformation. Lattice rotations have been tracked within grains yielding complex response behaviors that are being compared to model calculations. In the next year, we plan measurements that map not only to lattice orientations, but also elastic strain states with intra-granular resolution.

Element Specific Atomic Arrangement of Binary and Ternary Alloy Nanosized Catalysts in As Prepared and Active State

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

PROGRAM SCOPE

The objective of this research project is to characterize the atomic-scale structure of nanosized particle alloy catalysts in as prepared and active state under working conditions using element-specific synchrotron radiation techniques, such as high-energy resonant x-ray diffraction (XRD) coupled to differential atomic pair distribution functions analysis and three-dimensional atomistic simulations. The long-term impact of the project will be the development of well-defined and experimentally accessible atomic-scale structure based “benchmarks” for alloy NPs that are directly related to their catalytic properties.

FY 2012 HIGHLIGHTS

By conducting high-energy resonant XRD experiments, we demonstrated that contrary to theoretical predictions, Au and Pt do not phase segregate but alloy in particles less than 10 nm in size, resulting in the formation of catalyst that is very active for electro-oxidation of methanol [NanoLetters 12, 4289 (2012)]. Also, by conducting in situ XRD experiments, we found that Noble-Transition metal nanosized particles respond very differently when exposed to different gas environments. In particular, the particles expand in O_2-rich and shrink in H_2-rich atmospheres. The effect is substantial, amounting to 0.1 Å difference in the first neighbor atomic distances, and concurs with a dramatic change of the particles' catalytic activity [PRL 109, 125504 (2012)]. Furthermore, we showed that support-nanoalloy interactions influence very substantially the structural and chemical ordering in noble-transition metal nanoparticles, leading to support-tunable sites on the nanoalloys that are very active for oxygen activation in the catalytic oxidation of carbon monoxide [JACS 134, 15048 (2012)].

Ultrafast Magnetization Dynamics and Spin Transport Probed by Coherent Soft X-Rays

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Funding:	$318,000

PROGRAM SCOPE

The goal of this work is to capture the fastest dynamics relevant to function in magnetic materials using ultrafast coherent x-rays. Magnetism has been the subject of scientific inquiry for more than 2000 years, but it is still an incompletely understood phenomenon. The fundamental length and time scales for magnetic phenomena are nanometers (nm) and femtoseconds (fs). Furthermore, a detailed understanding of nanoscale magnetism has become much more critical in the 21st century with dramatic recent advances in magnetic data storage applications, since bits on a hard disk are already packed at scales of about 20nm. However, a comprehensive microscopic model of how spins, electrons, photons, and phonons interact does not yet exist. This understanding is fundamentally constrained in large part by our current very-limited ability to directly observe magnetism on all relevant time and length scales. Further advances in storage capacity and energy efficiency depend critically on a detailed understanding of the limits of magnetic switching speed and density. Until recently, measuring magnetic material dynamics used either ultrafast visible-wavelength lasers, or x-rays from large-scale electron storage facilities, such as synchrotrons and free electron lasers. Our work has shown that tabletop broad bandwidth high harmonic sources can simultaneously capture the instantaneous magnetic state of different elements in a magnetic alloy or in a multilayer, yielding surprising new understanding of spin transport and dynamics in nanosystems.

FY 2012 HIGHLIGHTS

We have three major highlights from 2012. First, we showed how the quantum exchange interaction that underlies ferromagnetism dictates how fast the magnetic state can be destroyed in alloys. Second, we showed that giant superdiffusive spin currents can be launched as a femtosecond laser and that these currents are directional, capable of increasing the magnetization of buried layers. Our findings shed light on a rich variety of new physics at play in femtosecond magnetization dynamics of technologically important magnetic alloys and multilayer systems.

Influence of Pressure on Physical Properties of Ammonia Borane Derivatives and their Re-Hydrogenation

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Funding:	$245,000

PROGRAM SCOPE

The goal of this project is to study behavior of high-potential candidates for on-board hydrogen storage materials, ammonia borane (NH_3BH_3) and its derivative lithium amidoborane ($LiNH_2BH_3$) at high pressures, and to understand the influence of pressure on their dehydrogenation process. Applying pressure to molecular crystals with weak intermolecular interactions may introduce a range of changes in atomic bonding and, in turn, produce crystal structure transitions. Using in situ x-ray diffraction and Raman spectroscopy, one can monitor changes in crystal structure and inter-atomic bonding. The project uses both diamond anvil cell and multi-anvil press in conjunction with the synchrotron x-ray source and the Raman spectroscopy system to study the crystal structure, phase stability, and inter-atomic bonding of these materials under high pressure and different temperatures, shedding a light on dehydrogenation and rehydrogenation process for hydrogen storage applications.

FY 2012 HIGHLIGHTS

We have investigated the phase stability of lithium amidoborane at pressures up to 13 GPa and 19 GPa using x-ray diffraction and Raman spectroscopy, respectively. Two pressure-induced phase transitions are identified. X-ray diffraction indicates that the first high pressure phase appears at about 4 GPa, and is stable up to about 10 GPa. Corresponding changes in Raman spectroscopy are also observed in the same pressure range. The first phase transition is accompanied by remarkable change in the B-H stretching region. The low frequency B-H stretching mode splits, and the high frequency B-H stretching modes merge into singlet. Also, notable change in optical image occurs at this phase transition. The sample is opaque to light before and it is transparent to light after phase transformation. The second phase transition is demonstrated by a merging of high frequency B-H stretching modes and a splitting of N-H stretching vibrational modes in the Raman spectra.

At ambient pressure, both the N-H and B-N Raman stretching modes of lithium amidoborane show blueshift to higher wavenumbers, whereas B-H stretching modes show redshift to lower wavenumbers, with regard to those of ammonia borane. This phenomenon indicates that lithium amidoborane has stronger N-H and B-N bonds and weaker B-H bonds than its parent compound, ammonia borane, which is consistent with the observation in the previous x-ray studies regarding the B-H and B-N bond length. In addition, unlike the pressure dependence of dihydrogen bonding characteristic Raman modes (i.e., the N-H stretching modes) in its parent compound, these N-H stretching modes in lithium amidoborane show a blueshift with increasing pressure. This is evidence that the dihydrogen bonding is likely absent in the lithium amidoborane structure.

Quantum Physics of Surface-Based Nanoscale Systems

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Funding:	$267,000

PROGRAM SCOPE

This program 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 prepared by deposition, artificial layering, self-assembly, and self-organization. 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 of such systems including the wave functions, total energy, electronic charge distribution, spin distribution, and density of states 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.

FY 2012 HIGHLIGHTS

Our recent work has made substantial progress in the investigation and understanding of (1) ultrathin topological insulator films, their interactions with substrates, and their surface chemical reactions; (2) competition between electronic and lattice effects on the epitaxial growth of thin films; (3) topological electronic transitions in metal films induced by substrate modulation; (4) dichroism associated with angle-resolved photoemission spectroscopy using circularly polarized light and the utility of this technique for surface spin texture mapping; and (5) pressure-induced phase transitions in the f-electron metal Ce.

Resonant Soft X-Ray Scattering Studies of Spontaneous and Engineered Electronic Order in Transition Metal Oxides

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Funding:	$261,000

PROGRAM SCOPE

The purpose of this project is to study the interplay between engineered nanoscale order, created artificially by nanofabrication techniques, and the innate electronic instabilities in transition metal oxides. Our long-term goal is to understand how these two types of order cooperate to create new types of collective behavior, with hopes of contributing in the long run to a revolution in strongly correlated electronic devices. By “electronic instabilities” we refer to spontaneous order like stripe phases, charge or spin density waves, orbital order, double-exchange ferromagnetism, or intrinsic electronic inhomogeneity due to proximity to a quantum critical point. The nanofabrication techniques used are atomic layer-by-layer growth with molecular beam epitaxy or pulsed laser deposition, areal patterning with electron-beam lithography, or thermodynamic self-organization. Of particular interest are the ground states that emerge at the interface between distinct strongly correlated oxides, or as a consequence of edge effects in nanoscale structures. The main experimental technique behind this project is resonant soft x-ray scattering (RSXS), which is one of the only techniques in existence that can selectively probe nanoscale valence, spin, orbital and lattice degrees of system, all with bulk sensitivity.

FY 2012 HIGHLIGHTS

Our progress in FY 2012 has been in three somewhat distinct areas: (1) theoretical efforts to determine an electron spectral function for RSXS; (2) reexamination of the ground state in the prototype, orbital ordering material $KCuF_3$; and (3) RSXS studies of the electronic structure of strongly correlated heterostructures, including epitaxial superlattices and mesoscale arrays.

Concerning the first area, we have recently shown that, under experimentally accessible circumstances, RSXS measures an electron spectral function very similar to that measured by ARPES and STM. This suggests a new direction for future studies of quasiparticles dynamics in copper-oxides. Concerning the second area, after several years of effort, both experimental and theoretical, we finally published a new perspective on the orbital state in $KCuF_3$, inverting many established beliefs based on the so-called “Kugel-Khomskii” model of orbital order. Finally, concerning the third area, we have completed studies of several new superlattice structures, including $LaMnO_3$-$SrMnO_3$, Sr_2CuO_4-La_2CuO_4, and La_2NiO_4-La_2CuO_4. We are evolving out of the superlattice subject, however, and are focusing in the future on mesoscale arrays of $La_{1-x}Sr_xMnO_3$, which show interesting collective order that we think may present a new strategy for creating new types of emergent quasiparticles.

Ultrafast Thermal Transport at Interfaces

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Funding: $375,000

PROGRAM SCOPE

The goal of this collaborative research project is to advance fundamental understanding of the ultrafast transport of thermal energy at material interfaces and to exploit these advances to provide new insights on interface structure and dynamics. Our work will encompass thermal transport at interfaces between single-crystal oxides, transport at interfaces between metals and molecular layers, and the development of new experimental methods; and will address the following long-term grand challenge.

How can we enhance the fundamental understanding of thermal transport at interfaces to better control the structure, bonding, and dynamics of material interfaces?

Our team will address this grand challenge through an interdisciplinary approach that brings together experts in thermal transport at the nanoscale and ultrafast optical metrology (Cahill); epitaxial growth of complex oxide crystals (Martin); and the synthesis of anisotropic metal nanostructures and control of their surface chemistry (Murphy). The combined expertise of our PI team will enable us to make progress on the grand challenges highlighted above. The outcomes of our research will be the development of model systems and experimental techniques that enable new generations of experimental studies of thermal transport at interfaces.

FY 2012 HIGHLIGHTS

We investigated the thermal relaxation of Au nanorods in two geometries: supported on crystalline substrates and suspended in water. When the pump and probe have the same wavelength, the thermal decays can be analyzed to extract the effective thermal conductivity of the 4-nm thick CTAB surfactant, ≈0.3 W/m-K. When the probe wavelength is blue-shifted relative to the probe, the decay in absorption appears to be accelerated, but this faster decay is actually caused by a contribution to the change in the absorption of opposite sign that comes from changes in the dielectric constant of the surfactant and water surrounding the nanorod. Thus, the transient absorption data does not depend only on the temperature of the nanorod but also has information about the changes in the temperature of the surroundings.

We grew thin epitaxial layers of ferroelectric oxides and measured how optical second harmonic generation (SHG) varies with steady-state temperature. The temperature dependence of SHG makes these ferroelectric layers a sensitive nanoscale thermometer in oxide heterostructures. The noise floor of the photodetector is approximately 0.1 μV/√Hz. Therefore, a ferroelectric layer with a thickness of only 4 unit cells should have a 100:1 signal-to-noise ratio. We are currently working to understand the limits of temporal and spatial resolution for this approach for ultrafast thermometry.

RECOVERY ACT - Generation, Imaging, and Control of Ultrafast Electrical Currents and Radiation

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Funding:	$150,000

PROGRAM SCOPE

The research objective is to investigate the physics of ultrafast electrical current and electromagnetic radiation generation/control in gaseous plasmas and solid-vacuum boundaries. In those systems, the PI and his team will use ultrashort 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 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.

FY 2012 HIGHLIGHTS

We have observed phase-matched terahertz generation in long air-plasma filaments produced by two-color photoionization. We find that phase matching naturally occurs due to off-axis constructive interference between locally generated terahertz waves, and this determines the far-field terahertz radiation profiles and yields. For a filament longer than the characteristic two-color dephasing length, it emits conical terahertz radiation in the off-axis direction. The total terahertz yield continuously increases with the filament length, well beyond the dephasing length. The phase-matching condition we observed provides a simple method for scalable terahertz generation in elongated plasmas. We have also observed new mechanisms responsible for terahertz polarization rotation and control in two-color filamentation. We find that the polarization of two-color laser pulses is greatly affected by self and cross Kerr nonlinearities. For non-parallel, two-color (400 nm, 800 nm) polarizations, the cross Kerr effect can greatly rotate the polarization of 400 nm, producing elliptically polarized terahertz radiation.

Optical Manipulation and Detection of Emergent Phenomena in Topological Insulators

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Funding:	$175,000

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 materials.

FY 2012 HIGHLIGHTS

We have demonstrated 3D band and spin mapping capabilities using time-of-flight based ARPES. We have also implemented an optical-pump 6eV ARPES probe setup that can record movies of 3D electronic band structure with femtosecond time resolution along with optical pump terahertz probe spectroscopy that can be performed in a magnetic field. Currently, we are working on implementing high harmonic generation that will enable varying our energy in ARPES between 10 ev and 100 eV. This will significantly increase our accessible momentum range and time resolution.

Ultrafast Electronic and Structural Dynamics in Quantum Materials	
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Funding:	$175,000

PROGRAM SCOPE

The three-dimensional topological insulator (TI) is a new quantum phase of matter that exhibits quantum-Hall-like properties, even in the absence of an external magnetic field. These materials are insulators in the bulk but have a topologically protected conducting state at the surface. Charge carriers on these surface states behave like a two-dimensional gas of massless helical Dirac fermions for which the spin is ideally locked perpendicular to the momentum. The purpose of this project is to probe the unique collective electronic behaviors of topological insulators by using advanced time resolved spectroscopic techniques with state-of-the-art temporal and spatial resolutions. Specifically, we will be focusing on three areas: (1) imaging topological spin currents and topological quantum phase transitions using spin sensitive time-and angle resolved photoelectron spectroscopy, (2) magneto-optical spectroscopy of topological insulators to study their anomalous magneto-electric quantization, and (3) non-linear ultrafast optical responses of topological insulators to study interface physics between topological and non-topological materials. These experiments offer the unique possibility to observe the macroscopic manifestations of topological quantum order in topological insulators for the first time, which is a crucial first step to understanding how they can be used for future energy efficient electronics, spin based processing devices, and fault-tolerant quantum computers.

FY 2012 HIGHLIGHTS

We have mapped 3D spin texture of topological insulators using circularly polarized light pulses to perform ARPES. We showed that there are deviations from ideal topological insulator behavior at high energies as predicted by theory. We have also managed to observe helicity dependent photocurrents from these materials by selectively coupling to different spin species. Using the time-resolved ARPES, we directly visualized in the momentum space how the surface and bulk electrons interact with each other.

We discovered that at high lattice temperatures, the coupling between the surface and the bulk is mediated through phonons and at low temperature, the coupling between the two is suppressed. At this regime, our experiments reveal that the helical Dirac fermions cool by emitting acoustic phonons. Currently, we are working on performing these experiments (both spin current and time-resolved ARPES) using excitation light pulses with energies below the bulk band gap. This will enable us to probe intrinsic response of the surface bands without any bulk contributions.

Nanoparticle Assemblies at Fluid Interfaces

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Funding:	$175,000

PROGRAM SCOPE

A quantitative understanding of the manner in which the nanoparticles assemble at the interface, the dynamics of the nanoparticles in the assemblies, and the kinetics of the assembly process is being investigated, but not fully understood. We are characterizing the interfacial assembly of nanoparticles, their dynamics, micelle formation and chemical activity of the nanoparticles by static scattering and reflectivity (neutron and x-ray) methods, coherent x-ray scattering, transmission electron microscopy, scanning force microscopy, and laser scanning confocal microscopy. In addition, the synthesis of functional organic and polymer ligands attached to the nanoparticles, and the design of new ligands to obtain a specific functionality are proposed. This will provide additional insight into the design of pathways to manipulate the assemblies, to optimize the functionality of the assemblies, and to tailor the ligands to control the assembly process. The ultimate objective of the research is to enable the generation of morphologies hitherto inaccessible using conventional routes by jamming nanoparticle at interfaces to kinetically trap morphologies in highly non-equilibrium states

FY 2012 HIGHLIGHTS

(1) Bjels: Spherical nanoparticles form a disordered monolayer at the interface; whereas rod-like particles, due to the shape anisotropy, formed ordered, monolayer domains and, with increasing concentration, can be forced to orient normal to the interface. With nanoparticles in a homogeneous mixture of two polymers and when the polymers underwent phase separation, the interfacial segregation of the nanoparticles arrested the phase separation process, freezing in the morphology in a highly non-equilibrium state. This arises from a jamming of the nanoparticles at the interface since, with time, the interfacial area decreases, to reduce the interfacial energy, causing the nanoparticles assembly to form a glass, prohibiting further area reduction and, therefore, freezing in the morphology. The interfacial segregation can be modified by controlling the chemical nature of the ligands and, in fact, can be forced into one of the domains. In this case, a percolated network within the domain formed, arresting a bicontinuous morphology.

(2) Dynamics of Nanoparticles at Fluid Interfaces: Using electric fields, fluid droplets were distorted or merged to change interfacial area forcing the assembly of nanoparticles to jam at interface. Synthetic routes were develop to enhance the interfacial energy to bind the nanoparticles at the interface, in particular by changing nanoparticles’ shape, generating Janus nanoparticles, and using ligand exchange.

The dynamics of nanoparticles were monitored by x-ray photon correlation spectroscopy (XPCS), optical microscopy and fluorescence microscopy. We measured with XPCS the dynamics of nanoparticles dispersed in the bulk and at the interface between two polymers.

Structure and Dynamics at Interfaces

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Students:	1 Postdoctoral Fellow(s), 2 Graduate(s), 2 Undergraduate(s)
Funding:	$171,000

PROGRAM SCOPE

The overall goal of this project is to better understand the behavior of epitaxial oxide heterostructures at atomic length scales (Ångstroms) and correspondingly short time-scales (fs -ns). The focus is structural and electronic correlations and how these can be exploited for the next generation of energy conversion and harvesting devices. Topics of interest include: mapping the atomic structure of heterointerfaces using x-ray surface scattering; using ultrafast lasers to study the effects of transient strain in coherent manipulation of multi-ferroic order parameters; and investigating structural ordering and relaxation processes in real-time. Studies of such processes are well matched to the capabilities of accelerator-based x-ray sources, such as the Advanced Photon Source at Argonne National Lab, and free-electron lasers, such as the Linac Coherent Light Source at Stanford Linear Accelerator Center. The broader goals of the proposed research are framed against the backdrop of the grand challenge of controlling matter and materials processes at the atomic scale. Of particular interest for this project is the behavior of materials which exhibit both electric and magnetic polarization, so-called multiferroic materials. $BiFeO_3$ is an interesting example which has a large spontaneous electric dipole moment and also antiferromagnetic ordering at ambient temperature. The interplay of these two types of ordering is of considerable interest in the context of correlated electron behavior as well as for potential device applications. Such behavior is well known in bulk ferroelectric and ferromagnetic materials; but the equivalent behavior in reduced dimensionality systems is only now being studied in some detail, for example, in thin-film and heterostructure materials. An important aspect of the methodology here is to utilize ultrafast time-domain pump-probe techniques to separate lattice and magnetic excitations in order to probe the fundamental questions of how lattice distortions and magnetization are coupled and what is the time scale of their relaxation.

FY 2012 HIGHLIGHTS

We have devised a new method to quantitatively determine the limits of resolution with which interfacial structures can be determined by surface x-ray scattering. This is important because subtle details of the structure, at the sub-Angstrom level, are key to understanding the physical basis of many intriguing interfacial phenomena in epitaxial thin films and nanostructures. X-ray phase retrieval methods are ideally suited to this task; but the usual approaches for determination of uncertainties, based on refining a parametrized model, are not applicable in this case. We have applied the method to cuprate oxide heterostructures which show novel interfacial superconductivity. We have shown that the approach is also useful in providing a quantitative measure of the validity of structural solutions obtained by x-ray phase retrieval methods.

Ultrafast Magnetization Dynamics and Spin Transport Probed by Coherent Soft X-Rays

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Funding:	$163,000

PROGRAM SCOPE

We seek to capture, image, and understand ultrafast, coupled, charge-spin-phonon transport and dynamics in magnetic materials using tabletop, laser-based, high harmonic (HHG) sources that can be used to capture the fastest dynamics in magnetic materials with elemental specificity. This work addresses grand-challenge science questions of understanding correlated matter and controlling matter at the level of electrons. We have four specific research thrusts: (1) generating spin current via ultrafast demagnetization—all-optical metal-based spintronics, (2) comparing spin scattering and exchange timescales in ferrimagnetic and ferromagnetic materials, (3) imaging spin current transport and domain dynamics, and (4) L-edge magnetic spectroscopy and imaging using HHG. The first topical thrust is motivated by our recent observation that optically-induced-demagnetization excites a spin-polarized population of hot carriers that carries angular momentum out of one magnetic layer and into a second magnetic layer at sub-100 fs timescales. Key questions we are now addressing are how the various mechanisms for demagnetization compete, since the laser excites all the layers in the multilayer, and what this tells us about the correlated interactions in magnetic materials. In the second thrust, we will explore exchange interactions in $(NiFe)_xCu_{1-x}$ alloys, where varying the Cu content modifies the exchange coupling in a continuous fashion. For the third thrust, we will combine our ability to capture magnetization dynamics with the coherent diffractive imaging techniques. This will build on the recent demonstration of 22 nm spatial resolution for topographical nanostructures. We will image spin scattering, spin transport, and domain dynamics in thin films, nanostructured and layered systems. In the fourth thrust, we will use recently-demonstrated HHG systems capable of generating keV photons to probe species-specific spin dynamics via L-edge contrast mechanisms. This will allow us to simultaneously image dynamics in Fe, Co, and Ni in a much wider variety of multilayer structures than what we have been able to study at the M-edge.

FY 2012 HIGHLIGHTS

We have used multilayers of Fe and Ni with different metallic and insulating spacers to show that we can control the competition between local spin-flip and non-local spin-current generation processes, and in some cases completely suppress interlayer spin-currents as the magnetic layers undergo rapid demagnetization. Our findings conclusively show that both spin-currents and optically-induced demagnetization due to localized spin scattering processes must contribute to ultrafast dynamics in magnetic materials. Finally, by reversing the order of the Fe/Ni layers, we demonstrated that spin-currents are directional in our samples, predominantly flowing from the top to the bottom layer.

Fundamental Studies of the Structural Response of Disordered Materials to High P and T

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Funding:	$176,000

PROGRAM SCOPE

The processing of many high value-added materials, including technical glasses and nano-materials, are manufactured via the liquid (molten or solution) phase. Increasingly industrial processing depends on the use of extreme conditions, supercritical solvents, such as water and CO_2, and nano-scale intermediates—all examples of disordered condensed matter. Our ability to follow the evolution of atomic arrangements in these materials in situ under simulated and real processing conditions is fundamental to manipulating physical properties. The utility of time-resolved high-energy x-ray diffraction (HE-XRD) and the complementary use of isotope-substitution neutron scattering are particularly important for disordered materials where the scattering is predominantly diffuse. The nature of the sample environment and sample cells that allows us to study materials in situ at high pressure (*p*), variable temperature (T), and electric field (E) places severe constraints on data quality, limiting our ability to constrain structure models. Innovative data analysis and modeling techniques, interfacing new sample cells with beamlines, will allow us to tackle important problems including the mechanism whereby novel solids absorb $CO_{2,}$ even in the presence of moisture, and the origins of the stability of water bridges formed when voltage gradients of greater then 10,000V are applied to containers filled with water.

FY 2012 HIGHLIGHTS

We have interfaced equipment with the high-energy 11-ID-C beamline at the Advanced Photon Source that allows us to collect real time data on water and solvent bridges stabilized in high voltage gradients. The initial results suggest that water tension, and not significant alignment of water molecules, is responsible for bridge stability. X-ray scattering experiments in our laboratories and at the Advanced Light Source, using high-pressure gas apparatus, revealed the location of CO_2 in a selective absorber of this gas. The solid's selectivity for CO_2, in the presence of moisture, is attributed to a novel interaction between the molecular quadrupole of CO_2 and a "π-pocket" formed by two phenyl rings. This is a new mechanism for sorption, not previously described.

Nanoscale Dynamical Heterogeneity in Complex Magnetic Materials

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Funding:	$147,000

PROGRAM SCOPE

A variety of nanostructured systems exhibit thermal- or field-driven intermittent behaviors that are a manifestation of nanoscale dynamical heterogeneity in a macroscopically homogeneous material. Ensemble dynamics of such systems often display complex and technologically important behaviors; for example, two level tunneling centers impact a host of low temperature thermodynamic properties in most glasses, jamming in colloidal systems leads intermittency and to stretched exponential kinetics and viscoelasticity, and superparamagnetic fluctuations in granular magnetic films limit the density with which information can be stored. Thermally driven intermittency limits the utility of a nanoscale device or nanostructured material to store, process, or transmit information; to sense the environment; to harvest and convert energy; and a host of other applications. The desire to control and to use nano-objects and nanostructured materials will often be limited by intermittency. The underlying hypothesis of our proposed research is that if we can probe, understand, and possibly control nanoscale intermittency, then we should be able to exercise some control over emergent material properties.

We apply resonant, coherent soft x-ray scattering techniques to probe nanoscale spatiotemporal correlations in magnetic films and transition metal oxides. Microscopic interactions in these systems support spontaneous domain structures on the scale of a few to a few hundred nanometers that produce unusual and useful macroscopic properties and that offer excellent models to probe complex, intermittent behaviors. Operating at soft x-ray wavelength in resonance with various absorption edges, we can probe nanoscale orbital, magnetic, and charge correlations with simultaneous elemental selectivity.

FY 2012 HIGHLIGHTS

We have discovered hidden, high order rotational symmetries in speckle patterns of magnetic domains in Co:Pd multilayers. These symmetries are remarkably sensitive to the illuminated domain pattern and exhibit correlated noise when the system is driven around the magnetization loop. We are starting to explore their relationship to field-driven Barkhausen cascades, with an eye toward learning to control intermittency.

Synchrotron X-Ray Based Study of Correlated Quantum Materials and Topological Insulators

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Funding:	$366,000

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 quarternary-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 in Oxides or the Weyl Fermions are underway.

FY 2012 HIGHLIGHTS

Demonstration of a new class of Topological Matter: A conventional topological insulator is protected by time-reversal symmetry. For example, the topological phase in the Bi1−xSbx system is due to an odd number of band inversions preserving time-reversal symmetry. A spin–orbit system, the Pb1−xSnxTe, has long been known in theory to contain an even number of inversions. We have recently demonstrated that a mirror symmetry-protected topological crystalline insulator phase is possible in the Pb1−xSnxTe class of materials which is unrelated to time-reversal symmetry. This also differs from the theoretically predicted compound SnTe. Our experimental results show that above the topological inversion phase transition, the surface exhibits an even number of spin-polarized Dirac cone states suggesting mirror-protected topological order distinct from that observed in all classic topological insulators such as Bi2Se3 or Bi1−xSbx. Our observation of the spin-polarized Dirac surface states in the inverted Pb1−xSnxTe and their absence in the non-inverted compounds related via a topological quantum phase transition provide the experimental groundwork for opening a new research-front on topological insulator research in quantum devices. Principal Publication*:* S.-Y. Xu et.al., *Nature Commun.* 3, 1192 (2012).

In addition, we have made a number of important advances in the understanding of quantum spin-orbital states of topological surface states in Bi-based (conventional) topological insulator materials originally identified by us.

Fundamental Mechanisms of Roughening and Smoothing during Thin Film Deposition

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Funding: $183,000

PROGRAM SCOPE

This project utilizes facilities at the X-21 beamline at Brookhaven National Laboratory to carry out time-resolved x-ray scattering studies of the evolution of surfaces during thin film growth. Over the last few years, theoretical studies have predicted that energetic particles that bombard surfaces as part of thin film deposition processes—such as sputter deposition and pulsed laser deposition—are responsible for the creation of ultra-smooth layers. Sputter deposition involves ion-erosion of a target composed of a selected material in a vacuum environment, where ejected atoms are deposited onto the surface of a sample placed nearby. Pulsed laser deposition is a similar process, using a laser pulse to ablate atoms from a target. In this project, we will test predictions for specific atomic-scale mechanisms using x-ray scattering studies to follow the dynamics of surfaces of thin films during the deposition process. The objective of the work is to develop an improved theory of roughening and smoothing of surfaces during thin film deposition, and in particular to extend models relevant to deposition of epitaxial films. The theme of nanostructured surfaces will also be extended to growth and characterization of epitaxial layers, with the objective of identifying the processes in deposition leading to pattern formation. Control and manipulation of smoothing processes on surfaces during thin film deposition are key challenges in technology and touch on a wide variety of applications that employ ultra-thin layers and nanostructured surfaces, or that exploit quantum effects to achieve desired electronic or magnetic properties. Examples include many types of photovoltaic, energy conversion/harvesting, and electronic devices.

FY 2012 HIGHLIGHTS

We have studied stress effects during pulsed laser deposition (PLD) and have observed submonolayer self-assembled islands forming in real time. Strained thin films have also been studied, and the transition from laminar to three-dimensional growth has been obtained for two different materials systems. Ongoing work will concentrate on identifying differences between PLD and sputter deposition, where significant differences in growth morphologies are observed. We have recently completed construction of a nanoparticle source based on a magnetron sputtering source, and will study the evolution of surface morphology of surface evolution during deposition from nanoparticles.

Photon-Electron Interactions in Dirac Quantum Materials

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Funding:	$150,000

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 topological insulators (TIs). These materials have unusual physical properties which hold promise for novel energy harvesting technologies. The proposed work will investigate the fundamental and technical aspects of graphene and TIs using the combination of ultrafast optical spectroscopy and electrical transport measurements. Such spatially and temporally resolved photocurrent measurements will allow us to explore new physical properties which are not accessible by either electrical transport or optical spectroscopy alone. Integrating these measurements with local material synthesis and device fabrication capabilities, we will perform rigorous investigations of energy transport by non-equilibrium Dirac quasiparticles, spatial transport and dynamics of topologically protected spins, and Berry-phase related photovoltaic effects. The resulting fundamental understanding of photon-electron interactions in nanoscale structures may lead to new energy-efficient applications including in low-power consumption and high-speed electronics and optoelectronics, dissipationless spintronics, plasmonics, and photovoltaics.

FY 2012 HIGHLIGHTS

Bi_2Se_3 is a well-known 3D topological insulator, which is insulating in the bulk but with gapless surface states protected by bulk-topology. Exotic optoelectronic response has been theoretically predicted in this new system, originated from the spin-momentum locking surface states. In our lab, we have applied spatially resolved photocurrent measurements to investigate the optoelectronic response of Bi_2Se nanowires, which has similar helical surface spin states as Bi_2Se_3 but without bulk topological protection. We found that there is interesting chiral edge photocurrent from Bi_2Se nanowires. The edge current can be further controlled by the polarization of the light. We attribute the new observation to the strong Rashba spin-orbtal coupling induced surface states. Our plan is to further investigate the optoelectronic response and its dynamics from topologically protected surface states.

Inelastic X-ray Studies of Highly Correlated Systems

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Funding:	$100,000

PROGRAM SCOPE

Our goal is to improve our understanding of strongly correlated condensed matter 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 the electronic and vibrational excitations in these systems. Our current work primarily involves developing polarization analysis for the scattered x-ray in RIXS. We designed and tested a toroidally bent graphite single crystal analyzer working at the copper K-edge, but the efficiency is low (1.5%). Currently, we are working on an analyzer for the iridium edge using bent, thin, high quality single crystal silicon. Over the last several years, iridium compounds have begun to attract significant interest due to their wide range of unusual properties.

FY 2012 HIGHLIGHTS

We have published our findings on the graphite polarization analyzer and begun work on higher efficiency thin (50 micron) single crystal silicon analyzers designed to study iridium compounds. After making the new analyzers, we have characterized the shapes using optical profiling. In addition, we have used x-ray topography to study the quality of the surfaces. Using these characterization techniques, we have come up with what we believe is a good fabrication method for analyzers. We will fully test the analyzers in the coming months.

Design of Molecular Solar Cells via Feedback from Soft X-Ray Spectroscopy

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

PROGRAM SCOPE

Spectroscopy with soft x-rays is used to assist the development of new materials and new designs for solar cells with better price/performance ratio. The starting point is the most general layout of a solar cell, which consists of an electron donor, a light absorber, and an electron acceptor. There are four relevant energy levels, which can be measured by a combination of x-ray absorption spectroscopy and photoelectron spectroscopy. This allows much more variation than a standard semiconductor solar cell, where only the band gap is variable. Research in 2012 has been focused on p-doped diamond films as inert donors and organic dyes with π systems as versatile absorbers, including molecules where all three components are combined in a single molecule (d-π-a complex).

In order to speed up the development of new solar cells, a feedback loop is envisaged between spectroscopy, theory, synthesis, and device fabrication. Spectroscopy of molecules and semiconductors provides input for theory, which helps explain the observed energy levels and their wave functions. First-principles DFT and TDDFT calculations have the capability to predict new materials of potential interest to photovoltaics. These blueprints are passed on to synthetic chemists and crystal growers with whom we collaborate. The newly synthesized materials are incorporated into device structures to test the electric performance. Since device processing may change the energy levels via interface reactions or creation of bulk defects, the ball comes back to spectroscopy.

FY 2012 HIGHLIGHTS

X-ray absorption spectroscopy has been performed at the ALS with Zn-porphyrin dyes customized with triphenylamine donor groups and carboxyl linkers to oxide acceptors [J. Electron Spectrosc. Relat. Phenom, published online (2012)]. By comparison with reference compounds, the orbitals of the donor and linker groups could be clearly distinguished from the π-system of the dye. First principles calculations with David Prendergast's group are under way to analyze the interaction of the donor groups with the π-system of the dye.

Spectroscopy of hematite photoanodes has been performed to link a dramatic enhancement of the photocurrent by annealing (x200) to changes in the electronic structure [J. Phys. Chem. C 116, 22780 (2012)]. The main change was found to be an outdiffusion of Sn from a SnO_2 underlayer into the Fe_2O_3. But more subtle changes were found as well, such as a reduction of gap states below the conduction band minimum.

Dynamics and Extreme Conditions in Complex Oxide Heterostructures

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Funding:	$196,000

PROGRAM SCOPE

Our research program focuses on the development and application of experimental tools to study the dynamics associated with the polarization and structure of complex oxide electronic materials. We focus in particular on physical phenomena arising from the interaction of structural distortion at interfaces and domain walls with the long-range electrical polarization of ferroelectric materials and new artificial layered structures derived from conventional ferroelectrics. The balance between competing effects results in the creation of novel ferroelectric domain patterns and makes these materials quite sensitive to the perturbation arising from externally applied electric fields. Because these phenomena have a fundamentally structural origin, we have developed a series of experimental techniques based around time-resolved synchrotron x-ray diffraction. We take advantage of the unique opportunity arising from the combination of nano-focused synchrotron x-rays with ultrafast techniques, and we combine these probes with an experimental capability to apply well-controlled external electric fields.

FY 2012 HIGHLIGHTS

Our work over the past year has focused on ferroelectric/dielectric superlattices. These are thin films consisting of alternating layers, with atomic-scale thicknesses, of ferroelectric and dielectric materials. In zero electric field, the electrical polarization in the superlattices forms a series of domains of alternating polarization. An applied field removes the domains and transforms the system into a uniform polarization state. We have developed x-ray diffraction techniques that allow us to probe this transition with nanosecond time resolution. With this approach, we have found that the transition occurs by a spatially heterogeneous process and that, at high electric fields, the entire transition can occur with a characteristic timescale of less than 10 ns [Phys. Rev. Lett. 107, 055501 (2011)]. A structural study of the superlattice in applied electric fields shows that, even within the striped domains, the structure is distorted by the field [Phys. Rev. Lett., in press (2012)]. In addition to this work with superlattice domain dynamics, we have probed the evolution of the atomic scale structure in uniform-composition ferroelectrics in which a domain pattern has been written using piezoelectric force microscopy and developed new techniques to allow high-resolution maps to be formed of the distortion of buried layers in epitaxial heterostructures.

Our future plans are to (1) determine how applied electric fields can induce other novel domain configurations in ferroelectric/dielectric superlattices, (2) combine optical pumping techniques with an x-ray nanoprobe in order to understand optically-induced phenomena in these superlattices, and (3) probe the dynamics of striped domains in superlattices at the 10-100 nm scale via coherent scattering.

Dynamics of Block Copolymer Nanocomposites

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Funding:	$189,000

PROGRAM SCOPE

The overall objective of this project is to establish and investigate the basic physical principles underlying the structures and dynamics within block-copolymers and block copolymer-nanoparticle nanocomposites. The new understanding achieved will facilitate the design and creation of robust and stable nanocomposites with desirable properties. In addition, we will provide new insight into the dynamics of neat block copolymer materials. To carry out this program, we will rely on synchrotron-based small-angle x-ray scattering (SAXS) and transmission electron microscopy (TEM) to determine the nanocomposite structures. To investigate the dynamics of these systems, we will employ x-ray photon correlation spectroscopy (XPCS) experiments at beamline 8-ID-I at the Advancd Photon Source at Argonne National Laboratory and at the LCLS at the Stanford Linear Accelerator Center. The results achieved will guide and facilitate future efforts to create and process designer nanocomposites for specific applications, for example, in such energy-related areas as batteries and solar cells.

FY 2012 HIGHLIGHTS

We refined our procedures for synthesizing poly(styrene-block-2 vinyl pyridine) micelles, henceforth P(S-b-2VP) micelles, decorated with CdS nanoparticles. To investigate the temperature-dependent structure and dynamics of BCPs decorated with these micelles, we incorporated P(S-b2VP) micelles with core-embedded CdS nanoparticles into bulk poly(styrene-isoprene), henceforth P(S-b-I), under the hypothesis that the micelles, which have PS shells, will be preferentially located in the PS-rich regions of the P(S-b-I) structure and may even self-organize in these regions, leading to a hierarchically-ordered material. To elucidate the nanostructure of the resultant blends experimentally, we carried out a series of electron microscopy measurements, which clearly reveal the locations of the CdS nanoparticles. Remarkably, there are several regions where clearly ordered patterns of CdS particles exist, showing that the parent BCPs are inducing nanoparticle order, consistent with our expectations.

We also carried out synchrotron-based SAXS and XPCS measurements on these materials. The SAXS profile of the neat P(S-b-I) is dominated by a characteristic disordered-phase peak at a wavevector of 0.034 Å^{-1}. By contrast, the blend shows a strong peak at 0.022 Å^{-1}, which must originate with the CdS nanoparticles because of their relatively strong scattering cross-section. The blend also shows a weaker peak near 0.034 Å^{-1}, which likely originates with the P(S-b-I) component of the blend. Our XPCS data determine the temperature- and wavevector-dependence of the relaxation time. The relaxation times increase rapidly as the temperature is decreased from 140 to 120°C, which may be attributable to microphase separation of the P(S-b-I) diblock copolymer, whose microphase separation transition occurs at 128°C in the melt.

DOE National Laboratories

Synchrotron Radiation Studies

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Funding:	$2,050,000

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 creative use of the Advanced Photon Source, the Wisconsin Synchrotron Radiation Center, and the Linac Coherent Light Source, we are developing 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. Our research probes novel phase transitions in ultra-thin ferroelectric films in chemical environments, where a new class of phase transitions in ferroelectrics with ionic surface compensation gives access to exotic non-polar and high-field states. We explore the competing interactions underlying high Tc superconductivity in order to understand their fundamental physics. We are developing surface coherent imaging techniques and applying them to understand 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 2012 HIGHLIGHTS

Using the Linac Coherent Light Source at SLAC, single ultrafast coherent x-ray pulses were used to observe the speckle contrast in the high-angle diffraction from liquid Ga and glassy Ni_2Pd_2P and B_2O_3. This work demonstrated that the source and optics are sufficiently stable for x-ray photon correlation spectroscopy studies of dynamics over a wide range of time scales. Using the Advanced Photon Source, we imaged nanoscale lattice strain in a SiGe-on-SOI device prototype with a new x-ray technique we developed, nanofocused Bragg projection ptychography. We measured the internal lattice behavior in a targeted region and demonstrated that its internal strain profile consisted of two competing lattice distortions. These results provide the strongest nondestructive test to date of continuum modeling predictions of nanoscale strain distributions. We studied the dynamics of the Au (001) surface in 0.1 M $HClO_4$ electrolyte solution using coherent surface x-ray scattering (CSXS). The steps and islands on the Au surface are highly dynamic in the electrolyte and move more than four orders of magnitude faster than in vacuum.

Towards Understanding and Control of Nano-Scale Fluctuations in Strongly Correlated Electron Systems

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Funding:	$1,200,000

PROGRAM SCOPE

The central focus of this project is 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 these and complementary techniques that are represented at Brookhaven for studying the same problem in a team environment involving Brookhaven scientists with similar interests. Nanoscale fluctuations are difficult to study but crucial to understanding the emergent properties of complex materials such as high-Tc superconductivity, colossal magnetoresistance, and 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 MBE synthesis.

FY 2012 HIGHLIGHTS

We are currently focusing on three systems: colossal magnetoresistant manganites, high temperature superconductors, and chalcogenide materials both with metal insulator transitions and with novel behavior that gives them excellent thermoelectric properties. A common theme that is emerging in all these materials is that competition between two states close in energy results in nanoscale modulations in structural, electronic, orbital, and magnetic order. The manganites are a model system where we are combining multiple techniques to understand the nanoscale fluctuations associated with the competition. We have imaged for the first time AFM domains using a recently developed soft x-ray resonant x-ray scattering technique. Surprisingly, the domains are of two distinct types where the order is the same but the spin orientation differs accompanied by an unexpected symmetry lowering. This occurs close to 50% doping where, using PDF, we clearly see the coexistence of localized insulating and delocalized metallic clusters on the nanoscale on cooling in PDF and TEM. The main result in the chalcogenides is the discovery of a local disordered dimer state in a nominally un-dimerized and metallic part of the phase diagram of Cr doped $CuIr_2S_4$. This has multiple charge and orbitally ordered states associated with metal-insulator transitions that we now know can only be understood by studying the presence or absence of local dimers that are not long-rang ordered. In the thermoelectric chalcogenides, we are studying the effect of doped disorder on local fluctuating dipole state that we discovered in 2010. Again, we believe that competition between two states, displaced and non-displaced, is at the heart of this rich behavior. In the stripe-ordered nickelate system, which we are treating as a model system for studying local broken symmetry states in the cuprates, we have mapped out the region of phase space where short-range ordered stripe correlations may be found above the charge-ordering temperature. On the methodological side, we demonstrated how to obtain quantitatively reliable PDFs from electron diffraction data and ran the first experiments on X17A beamline at NSLS.

X-Ray Scattering

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Students:	1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$1,195,000

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 state-of-the-art 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 long-term goals of understanding and ultimately controlling the properties of these materials. The program seeks to address questions on the mechanisms of high-temperature superconductivity and the role of intrinsic perturbations in strongly correlated systems and to understand the dynamics of these systems over a wide range of time and energy scales. Inelastic and elastic x-ray scattering experiments will be carried out as part of a broader effort within CMPMSD and more generally at 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. It is involved in the development and use of two sectors at the Advanced Photon Source and four beamlines at the NSLS-II.

FY 2012 HIGHLIGHTS

We are presently focusing on the electronic dynamics of 3*d* and 5*d* transition metal oxides. The 5*d* oxides offer an exciting new perspective on their more familiar 3*d* cousins, and have the additional feature of large spin-orbit coupling, which mixes the spin and orbital degrees of freedom. In the past year, we have studied a model iridate Sr_3CuIrO_6, specifically focusing on the magnetism. We have shown that there are indeed well-defined moments in this system and that the exchange pathways generate novel magnetic behavior because it is a mixed 3*d*-5*d* system, resulting in, for example, ferromagnetic anisotropy from ferromagnetic exchange. We have also carried out the first studies of a doped iridate, namely $Sr_{0.95}La_{0.05}IrO_4$. Relative to the undoped parent, we find the magnons are broadened and significantly softened, presumably because the dopants introduce additional scattering mechanisms. Finally, we have been studying $Na_4Ir_3O_{8,}$ a candidate 3D quantum spin liquid. A broad low-energy, non-dispersive continuum is observed extending up to 500 meV. Analysis of this continuum is ongoing. In work on the 3*d* transition metal oxides, we have studied the local charge screening dynamics in a manganite, $La_{1.5}Sr_{0.5}MnO_4$. We find that these are strongly momentum-dependent and that this reflects a highly-localized nearest-neighbor screening. We estimated the screening cloud to be approximately 0.5 atomic distances in size in this system.

Fundamental Structural Studies of Hybrid Biomolecular Materials using Scattering Technologies

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Principal Investigator:	Xu, Ting
Sr. Investigator(s):	Kortright, Jeffrey, Lawrence Berkeley National Laboratory Francis, Matthew, Lawrence Berkeley National Laboratory
Students:	1 Postdoctoral Fellow(s), 3 Graduate(s), 0 Undergraduate(s)
Funding:	$250,000

PROGRAM SCOPE

This program carries out structural studies on the hierarchical assemblies of two families of biomolecular building blocks—*de novo* designed helix bundle peptide-polymer conjugates and chemically-engineered viruses. Synthetic routes will be developed to synthesize peptide-polymer conjugates with well-defined architectures and viruses with site-specific protein modification. Various scattering techniques using synchrotron and neutron sources will be used to elucidate the assemblies at multiple length scales with a focus to obtain fundamental understanding of the phase behavior of peptide/protein and polymers and the parameters dictating the assembly process. Soft x-ray scattering techniques will be explored to study the nanostructures of peptide-containing biomolecular materials. Using *de novo* designed photoactive peptide-polymer conjugates and chemically-modified TMV as examples, the fundamental principles emerging from this program should be applicable to other building blocks; and functionalities can be readily incorporated by varying building blocks. These research efforts will not only enrich our fundamental understanding in phase behavior of biomolecular building blocks, but also pave the path to generate functional materials with properties similar or superior to those seen in nature.

Ultrafast Materials Science Program

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Principal Investigator:	Schoenlein, Robert
Sr. Investigator(s):	Kaindl, Robert, Lawrence Berkeley National Laboratory Orenstein, Joseph, Lawrence Berkeley National Laboratory Lanzara, Alessandra, Lawrence Berkeley National Laboratory
Students:	4 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$1,715,000

PROGRAM SCOPE

This program applies advanced ultrafast techniques to fundamental problems in condensed matter physics. The focus is on complex materials where correlation among charges and between charge, spin, and phonons lead to new properties, quasiparticles, and exotic phases; and novel physics at interfaces and in nanostructured materials. Ultrafast spectroscopy provides new insight by separating correlated phenomena in the time domain with resolution shorter than the underlying coupling processes. The program consists of four coupled research areas: (1) understanding charge, spin, and quasiparticle dynamics via THz spectroscopy and time-resolved four-wave mixing; (2) understanding magnetization dynamics via transient spin grating and magneto-optic Kerr spectroscopy; (3) understanding cooperative phase transitions, critical phenomena, and electron phonon coupling via ultrafast visible and mid-IR spectroscopy; and (4) understanding atomic and valence-electronic structural dynamics in complex materials via ultrafast VUV/EUV angle-resolved photoemission and x-ray spectroscopy. Measurements of correlated phenomena on fundamental time scales, at atomic spatial scales, with momentum resolution and element specificity are indispensable for achieving new insight into the emergent physics of complex materials and nanostructures.

FY 2012 HIGHLIGHTS

Manganites are a model system for understanding the coupling mechanisms between competing electronic ground states which underpin colossal magnetoresistance and other exotic phenomena. Our time-resolved resonant soft x-ray scattering studies in $Pr_{0.7}Ca_{0.3}MnO_3$ reveal the glass-like physics that mediate the dynamics of antiferromagnetic spin ordering. Moreover, the observed dimensional crossover in the interaction from 1D to 3D as a function of pump fluence suggests that spin ordering and orbital ordering are transiently decoupled by photo-excitation. The nickelates are isostructural to cuprates yet exhibit charge stripes without superconductivity. Our observation of a mid-IR pseudogap in $La_{2-x}Sr_xNiO_4$ at a temperature far above that of stripe formation manifests the development of fluctuating short-range charge order. Our ultrafast mid-IR studies of the gap dynamics reveal the transient decoupling of charge order and lattice vibrations, establishing a primarily electronic origin of stripe correlations and the mid-infrared pseudogap in nickelates. Our time-resolved optical studies of the itinerant helimagnet $Fe_{0.8}Co_{0.2}Si$ reveal distinct periodic magnetic excitations that disperse to lower frequency with applied magnetic field. This is a characteristic signature of helimagnons, which are collective modes unique to helimagnets. In the next period, we will apply advanced ultrafast optical and x-ray techniques to understand the dynamics of collective modes in a range of complex materials.

Ultrafast Optical Spectroscopy: Investigating Dynamic Correlations in Complex Materials

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Principal Investigator: Trugman, Stuart A.
Sr. Investigator(s): Prasankumar, Rohit, Los Alamos National Laboratory
Students: 1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding: $300,000

PROGRAM SCOPE

A coupled theoretical/experimental approach is used to explore quasiparticle excitation and relaxation/recombination processes in complex materials. Specific materials studied include multi-layered cuprate superconductors and hybridization-gapped heavy fermions to understand quasiparticle relaxation and recombination in the presence of gaps or pseudogaps that arise as the result of interactions; ferroelectrics and multiferroics to investigate the role of competition and coexistence of ferromagnetic, antiferromagnetic, and ferroelectric order parameters; and organics, transition metal oxides, and manganites to study polaron formation and their coupling to other quasiparticles.

FY 2012 HIGHLIGHTS

We completed a fundamental study of the relaxation dynamics of the Holstein polaron (Golez, Trugman et al., *Physical Review Letters,* in press, arXiv:1209.2586). Keeping fully quantum phonons and electrons, we have computed the relaxation time of the Holstein polaron after it is driven far from the equilibrium by a strong electromagnetic pulse. Just after the pulse, the polaron's kinetic energy increases and subsequently exhibits a relaxation type decrease with simultaneous emission of phonons. In the weak coupling regime, partial tunneling of the electron from the polaron self-potential is observed. The inverse relaxation time for small values of the electron phonon coupling is linear in λ, while it deviates downwards from the linear regime at λ >_ $0.1/\omega_o$, where ω_o is the phonon frequency. Further, the imaginary part of the equilibrium self-energy shows good agreement with the inverse relaxation time obtained from nonequilibrium simulations.

Using a coupled theoretical/experimental ultrafast optical spectroscopic approach, we investigated carrier dynamics in the heavy-fermion compound URu_2Si_2 from 5 to 300 K (Liu, Trugman et al., *Phys. Rev. B* (2011)). The amplitude and decay time of the photoinduced reflectivity increased in the vicinity of the coherence temperature $T* \sim 57$ K, consistent with the presence of a hybridization gap. At 25 K, a crossover regime manifests as a new feature in the carrier dynamics saturating below the hidden-order transition temperature of 17.5 K. This is indicative of a pseudogap region (17.5 K < T < 25 K) separating the normal Kondo-lattice state from the hidden-order phase. Rothwarf-Taylor modeling of the data yields values of ~10 meV for the hybridization gap and 5 meV for the hidden-order gap.

Scattering and Microscopy with X-Rays and Neutrons

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Sr. Investigator(s):	Ice, Gene, Oak Ridge National Laboratory Specht, Eliot, Oak Ridge National Laboratory Pang, Judy, Oak Ridge National Laboratory Barabash, Rozaliya, Oak Ridge National Laboratory
Students:	0 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$1,675,000

PROGRAM SCOPE

This goal of this project is to understand the underlying physics of materials and processes of importance for energy technologies, specifically using x-ray and neutron scattering. New insight will be obtained into how domain formation, local stresses, and phase coexistence give rise to emergent structural, electronic, and magnetic properties in materials. An increased emphasis on neutron scattering research will include the development and the application of neutron microfocusing optics at the Spallation Neutron Source. Scattering studies of local structure and magneto-volume effects in 3*d* and high-entropy alloys will be initiated. Nondestructive x-ray microscopy with 3D submicron resolution is used to probe long-standing issues in materials physics, including elastic and plastic deformation, 3D grain growth, and phase-separated microstructures in complex transition metal oxides. Central to the approach is the use of innovative, spatially-resolved neutron and x-ray scattering techniques coupled with advanced theory and modeling. High-brilliance APS synchrotron beams will enable the development of sub-100-nm x-ray diffraction microscopy, and high intensity SNS neutron beams will enable sub-50-µm neutron probes. Direct connections between scattering measurements and theory and modeling made possible by this program are critical for the development of a predictive understanding of materials behavior.

FY 2012 HIGHLIGHTS

Research efforts in FY 2012 have led to advances in understanding how local microstructure and heterogeneities such as defects and strain distributions control the physical properties of materials. This research has included the development of new “nested-mirror” concepts and techniques for x-ray and neutron focusing optics at the Advanced Photon Source and Spallation Neutron Source that enable spatially-resolved scattering studies of local microstructure and evolution. These three-dimensional (3D) experimental studies have been used to quantitatively test and guide theoretical models, and hence have provided a more fundamental understanding of microstructural evolution associated with crystal plasticity, grain interactions, and phase transitions. In particular, investigations of the microstructural origins of mechanical properties over multiple length scales employed x-ray microdiffraction and diffuse scattering measurements to study structural metals: 3D micron-resolution studies of deformation microstructures in fcc metals and high-entropy alloys; interface strength and strain gradients near buried interfaces in two-phase alloy composites; and 3D mesoscale investigations of the role of boundary mobilities and local dislocation densities during thermal grain growth. Focused x-ray microdiffraction was also employed to investigate the effects of local inhomogeneities on physical properties of nanostructured oxide materials. Spatially-resolved investigations revealed how microstrain distributions control phase separation and evolution during the classic metal-insulator phase transition in vanadium dioxide.

Electronic and Magnetic Structure of Quantum Materials

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Sr. Investigator(s):	Devereaux, Thomas, SLAC National Accelerator Laboratory Moore, Robert, SLAC National Accelerator Laboratory Hashimoto, Makoto, SLAC National Accelerator Laboratory Lu, Donghui, SLAC National Accelerator Laboratory Kirchmann, Patrick, SLAC National Accelerator Laboratory
Students:	5 Postdoctoral Fellow(s), 8 Graduate(s), 0 Undergraduate(s)
Funding:	$2,278,000

PROGRAM SCOPE

Quantum materials research represents an exciting opportunity to advance our understanding of grand scientific challenges and to impact future energy technologies. The multiple degrees of freedom from spin, charge, orbital, and lattice often conspire to give rise to remarkable emerging properties. We propose a comprehensive program to tackle this important but complex problem through a "complete set" of ARPES experiments that includes energy, momentum, spin and time resolution, further complemented by in-situ materials synthesis and theoretical investigation. ARPES has grown to one of the important techniques in the modern study of quantum materials and is now recognized as an essential contribution in the path towards a fundamental understanding of materials properties. The proposed program will bring many new dimensions to our ARPES experiments and theory of spectroscopy, thus elevating the expected level of impact. The new experimental capabilities include the following: (1) new beamline with improved flux, resolution, polarization control, and spectral range; (2) pico-second laser based high (spectral) resolution ARPES system; (3) femto-second laser based tr-ARPES system; (4) sr-ARPES system; and (5) in-situ materials synthesis capability. At the same time, improvements in computational methods and architectures have enabled highly accurate simulations of photon-based spectroscopies often able to connect quantitatively with measured spectra. We select four scientific areas to focus: novel superconductivity; novel orbital, spin, and spin-orbit physics; quantum systems in low dimension; and non-equilibrium physics. This synergetic mixture of science drivers and experimental tools promises the best opportunity to attack the "problems of scale" presented by the complexity of quantum materials.

FY 2012 HIGHLIGHTS

Our collaborative research resulted in 12 high profile papers. We continue to make important progresses towards understanding cuprate superconductors, highlighted by a number of high profile papers elucidating the relationship between the so-called pseudogap and the superconducting gap [Science, 331, 1579 (2011); Phys. Rev. Lett. 106, 167003 (2011); Phys. Rev. Lett., 107, 127003 (2011)]. We are making strides in understanding the Fe-pnictide superconductors [PNAS, 108, 6878 (2011)] and topological insulators and their potential applications [Nanture NanoTech 6, 705 (2011); Nature Chemistry, 4, 281 (2012)]. We have also made a number of important discoveries on the novel surface properties of complex oxides [Nature Materials, 10, 114 (2011); Phys. Rev. Lett., 108, 117602 (2012)].

We have also made progress in developing time and angle-resolved photoelectron spectroscopy and applied it successfully to the study of topological insulators [Phys. Rev. Lett., 108, 117403 (2012)].

Interfaces and Catalysis for Energy Conversion and Storage

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Sr. Investigator(s):	Toney, Michael, SLAC National Accelerator Laboratory Ogasawara, Hirohito, SLAC National Accelerator Laboratory Friebel, Daniel, SLAC National Accelerator Laboratory Kaya, Sarp, SLAC National Accelerator Laboratory Chueh, William, Stanford University
Students:	5 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$879,000

PROGRAM SCOPE

This program addresses chemical transformations involving solid-liquid interfaces where electrocatalysis occurs. Many of the essential processes in energy conversion, energy storage, and reduced energy impacts on the environment involve chemical transformations at interfaces between solids and electrolyte solutions or gases. Our effort is related to the DOE Grand Challenge of understanding the “nano-scale communication” and “control of electrons” in interfacial problems. The program consists currently of two subtasks with focus on the usage of x-rays to characterize materials connected to interfacial processes in fuel cell catalysis and for hydrogen storage under extreme environments.

FY 2012 HIGHLIGHTS

Highlights regarding the development and mechanistic characterization of alloy fuel cell catalysts include the following: (1) In-situ anomalous SAXS has been used to probe the composition and particle size dynamics in Pt-alloy nanoparticle electrocatalysts. (2) Studies using APPES to test O/Pt(111) interactions under systematic variation of O2, H2O, and H2 pressures continue. The new XPS cell is being used probe the Pt/electrolyte/gas triple phase boundary in a true potential-controlled three-electrode setup, and in the two electrode configuration of a working fuel cell. (3) In collaboration with Jens Nørskov, DFT and Monte-Carlo simulations are being used to predict adsorbate coverages as function of potential on different model surfaces. (4) In situ HERFD XAS and EXAFS have been employed to study small Pt nanoparticles. We have compared the O/OH chemisorption strength and the degradation (oxide formation, dissolution) with the previously studied single-crystal model systems Pt/Rh(111) and Pt/Au(111).

Highlights regarding the bonding and structures of light element-hydrogen systems under extreme conditions include the following: (1) Hydrogen storage in ammonia borane: In collaboration with theorists at Wake Forest, we solved the crystal structure of the new phases discovered in the ammonia borane. This work was published in *J. Phys. Chem*. earlier this year. (2) Super-hard carbon-rich materials: Using x-ray Raman scattering and x-ray diffraction, we found a pressure-induced sp2-to-sp3 conversion in glassy carbon which was complete above 40 GPa. Our findings expand the wealth of pure carbon allotropes and offer exciting possibilities for potential applications using pressure-dependent super-hard, amorphous solids and was published in *Phys. Rev. Lett.* in 2011. (3) Pressure induced stabilization of antiferromagnetic phase in Nd0.53Sr0.47MnO3: High pressure x-ray magnetic circular dichroism and neutron diffraction measurements provide the first experimental evidence for the presence of antiferromagnetic domains within the conducting ferromagnetic host of Nd0.53Sr0.47MnO3 at ambient pressure. This work was submitted to *Phys. Rev. Lett*.

Magnetization and Dynamics

Institution:	SLAC National Accelerator Laboratory
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Principal Investigator:	Durr, Hermann
Sr. Investigator(s):	Stohr, Joachim, SLAC National Accelerator Laboratory Moler, Kathryn, Stanford University Hoffmann, Matthias, SLAC National Accelerator Laboratory Kirtley, John, Stanford University
Students:	1 Postdoctoral Fellow(s), 3 Graduate(s), 0 Undergraduate(s)
Funding:	$1,398,000

PROGRAM SCOPE

This program seeks to understand the ultimate time scale for magnetic switching in nanomagnets which will set the limits of future devices and structures for both biomedical and information technology applications. An understanding of the complex interactions between electronic, spin, and lattice degrees of freedom, and how they play out in the relevant interactions in magnetic solids such as Coulomb, exchange, spin-orbit, and electron-phonon interaction, will enable the engineering of such devices and structures for optimum performance. The main goal of this research is to learn how to manipulate/control ferromagnetism using LCLS, SSRL, and Squids (complementary time and length scales) to determine speeds for magnetic switching and to characterize transient spin states far from equilibrium.

The program subtasks address a combination of ultrafast scattering and imaging (XMCD, PEEM) capabilities using the LCLS and SSRL unique and complementary light sources with fs and ps capabilities, respectively, along with the magnetic characterization using scanning-probe-based magnetic imaging, particularly scanning SQUID microscopy. XMCD and SQUIDs provide complimentary information in that XMCD provides chemically specific (spin and orbital) magnetic moment mapping, while SQUIDs measure the total local magnetization. As ultrafast and ultrashort timescale and ultra-small length scale are the frontiers of magnetism research, this teaming will enhance the productivity of both aspects because they are intellectually linked.

FY 2012 HIGHLIGHTS

Work since 2010 has focused strongly on LCLS, the world's first x-ray free electron laser. This resulted in demonstrating the single-shot imaging possibility for magnetic solids, the discovery of emerging novel ferromagnetic order during far from equilibrium conditions in metallic CoFeGd ferrimagnets, and the intimate electron-lattice coupling during the insulator to metal transition in magnetite. Work at SSRL and ALS led to visualizing the importance of charge and spin fluctuations during phase transitions that unfold both in equilibrium and in the time domain. The combination of synchrotron and laboratory based imaging techniques led to the identification of magnetic dipoles at the interface of strongly correlated oxide materials that are otherwise non-magnetic.

Spin Physics

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Principal Investigator:	Zhang, Shoucheng
Sr. Investigator(s):	Manoharan, Harindran, Stanford University
Students:	3 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$415,000

PROGRAM SCOPE

The Spin Physics program investigates novel phenomena arising from spin-orbit coupling in solids. In conventional semiconductors, spin-orbit coupling gives the possibility of electric manipulation of the spin degrees of freedom, which can be used for data storage and information processing. More recently, it is 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 2012 HIGHLIGHTS

Our theory group has successfully predicted 2D and 3D topological insulators in HgTe and Bi2Te3 systems. In these systems, spin-orbit coupling of the heavy elements play a dominant role and the interaction effects can be neglected. The field is now focused on topological Mott insulators, where the interactions play a crucial role. We proposed that the actinide materials PuTe and AmN could be topological Mott insulators, only when interaction effects are take into account [Science 335, 1464 (2012)]. If confirmed, this would be the first interacting topological insulator observed in Nature. Our theory group also actively works on theoretical predictions on novel effects of topological insulators, including the topological p-n junction, the quasi-particle interference on the surface of TI, and helical modes on the surface of weak Tis. The Orenstein group made significant progress in understanding the fundamentals of spin dynamics in spin-orbit coupled electron gases [Phys. Rev. Lett. 106, 247401 (2011); Nature Physics 8, 153-157 (2012)]. The Manoharan group made significant progress this year in STM/STS and atomic manipulation studies of new quantum materials and spin/pseudospin-based topological ground states, including the first “designer” Dirac fermions synthesized by transforming normal surface states on Cu(111) into hosts for massless Dirac fermions [Nature 483, 306–310 (2012); Physics Today 65, 76 (2012)]. Goldhaber-Gordon’s group has also been developing a novel probe of electron organization in buried 2D electron systems, which serve as clean, tunable models for correlated electron behavior [Appl. Phys. Lett. 97, 132103 (2010)].

Time-Resolved Soft X-Ray Materials Science at the Linac Coherent Light Source and the Advanced Light Source

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Principal Investigator: Devereaux, Thomas
Sr. Investigator(s): Hussain, Zahid, Lawrence Berkeley National Laboratory
Lindenberg, Aaron, Stanford University
Reis, David, SLAC National Accelerator Laboratory
Moore, Robert, SLAC National Accelerator Laboratory
Trigo, Mariano, SLAC National Accelerator Laboratory
Mao, Wendy, Stanford University
Shen, Zhi-Xun, SLAC National Accelerator Laboratory
Students: 9 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding: $1,772,000

PROGRAM SCOPE

The purpose of this research is to develop a world class program on the dynamics of complex materials using the soft x-ray beamline available at the Linac Coherent Light Source (LCLS) at SLAC to address the grand challenge problems of “emergence” and nonequilibrium dynamics, and to develop model systems for deep insights on materials for energy conversion, transport, and efficiency. We propose performing time-resolved, optical-pump and ray probe, momentum-resolved x-ray scattering on strongly correlated materials utilizing the ultra-short soft x-ray pulse produced by the SXR beamline of LCLS, table-top laser measurements, and diamond anvil cell x-ray scattering techniques. Theoretical calculations will be performed in parallel to gain further insight into the experimental data and establish formalism for describing non-equilibrium physics of strongly correlated materials.

FY 2012 HIGHLIGHTS

Since its completion, we have actively participated the commissioning of the soft x-ray material science (SXR) beamline at the LCLS. Publications regarding these commissioning experiments include general SXR beamline characterizations [W. F. Schlotter et al., Rev. Sci. Inst. 83, 043107(2012)], temporal cross-correlation between x-ray FEL and pump laser [M. Beye et al., Appl. Phys. Lett. 100, 121108 (2012) and O. Krupin et al. Optics Express 20, 11396 (2012)], and the RSXS endstation [D. Doering et al., Rev. Sci. Inst. 82, 17620 (2011)]. These commission results provide verified specifications of the SXR beamline and place general guidelines for the future experiments to follow.

A new pathway to melt electronic order was revealed via time-resolved pump-probe resonant x-ray diffraction using the RSXS endstation and femtosecond x-ray FEL at the LCLS. In our experiments on charge striped nickelate, La1.75Sr0.25NiO4 [W. S. Lee et al. Nature Communications 3, 838 (2012)], the charge and spin order can be significantly suppressed after photo-excitation by pump laser pulses. Surprisingly, the correlation length and the period of the charge order remain unchanged within the investigated time windows, distinct from the thermal melting process. Similar behaviors have also been observed in the magnetic order of copper oxide (CuO) [S. L. Johnson et al., Phys. Rev. Lett. 108, 037203(2012)] and manganite (La0.5Sr1.5MnO4) [M. Först et al., Phys. Rev. B 84, 241104(R) (2011)].

We completed first experiments at the LCLS hard x-ray pump-probe endstation probing ultrafast structural dynamics in PbTiO3 oxide nanolayers. These measurements led to new understanding of the photovoltaic response of these materials, and further enabled new understanding of the coupled electronic and structural dynamics that exist in ferroelectric and multiferroic thin films. These measurements make use of laboratory-scale THz sources as well as the fields generated by the SLAC linac. Work characterizing the amplitude of these fields was completed in early FY2012 and published recently [Daranciang et al. Appl. Phys. Lett. 99, 141117 (2011)].

II. CHEMICAL SCIENCES, GEOSCIENCES, & BIOSCIENCES DIVISION

AMO Sciences

Institutions Receiving Grants

Coherent and Incoherent Transitions

Institution:	Auburn University
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Principal Investigator:	Robicheaux, Francis
Sr. Investigator(s):	
Students:	1 Postdoctoral Fellow(s), 0 Graduate(s), 4 Undergraduate(s)
Funding:	$90,000

PROGRAM SCOPE

This theory project focuses on the time evolution of systems subjected to either coherent or incoherent interactions. 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. We have used these techniques to study the correlation between two (or more) continuum electrons and electron impact ionization of small molecules.

FY 2012 HIGHLIGHTS

We developed a method for solving the time-dependent Schrodinger equation for two electrons in extreme circumstances. Borrowing ideas from discrete variable theory (extensively used in chemistry calculations), we were able to efficiently evaluate the action of the $1/r_{12}$ operator on the wave function. We could propagate the fully three-dimensional wave function for two electrons up to the largest number of coupled angular momenta we tested (160). We used this propagator as the basis for a method to study the Ne system (photoionization with subsequent Auger decay). We found that the quantum calculation could reproduce all aspects of the experiment. We used the quantum wave function to understand why the classical calculations did not give the experimental result.

We performed two studies of atomic processes in strong magnetic fields partially motivated by recent experiments that have demonstrated trapping of anti-hydrogen atoms. The first study was a classical and quantum investigation of the ionization of Rydberg H atoms by a slowly ramped electric field which is commonly used to measure the energy distribution of Rydberg states (state selective field ionization). In a separate study, we investigated the charge exchange that occurs when positrons scatter from Rydberg atoms. We found that the transfer rate scales as $T^{1/2}$ for low temperatures but is substantially below this at higher temperatures.

We were involved in two projects to study high harmonic generation in special circumstances. We investigated the enhancement of HHG in the presence of noise by solving the non-perturbative stochastic time-dependent Schrodinger equation. We used the resulting wave function to quantify how varying noise levels affect the frequency components of the high harmonic spectrum. In some cases, a factor of ~50 enhancement can be achieved in the yield near the cut-off region. We also observed an effect due to carrier envelope phase for weak noise. We investigated the generation of a broad XUV continuum in HHG by spatially inhomogeneous fields. For some cases, we were able to increase the plateau region by roughly a factor of 2. We found that the field inhomogeneity plays a critical role in quantum path selection.

Imaging Multi-Particle Atomic and Molecule Dynamics

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Principal Investigator:	Landers, Allen
Sr. Investigator(s):	
Students:	0 Postdoctoral Fellow(s), 2 Graduate(s), 2 Undergraduate(s)
Funding:	$120,000

PROGRAM SCOPE

We are investigating phenomena associated with ionization of an atom or molecule by single photons (weak field), with an emphasis on ionization-driven atomic and molecular dynamics. Of particular interest is untangling the complicated electron-correlation effects and molecular decay dynamics that follow an initial photoionization event. We perform these measurements using variations on the well-established cold target recoil ion momentum spectroscopy (COLTRIMS) technique. The experiments take place at the Advanced Light Source at LBNL as part of the ALS-COLTRIMS collaboration with the groups of Thorsten Weber at LBNL and Reinhard Dörner at Frankfurt. Because the measurements are performed in “list mode” over a few days where each individual event is recorded to a computer, the experiments can be repeated virtually with varying gate conditions on computers at Auburn University over months. Participation in the experiments and performing the associated complicated analysis constitutes the majority Auburn effort. We continue to collaborate closely with theoreticians also funded by DOE-AMOS, including most recently, the groups of F. Robicheaux and C. W. McCurdy.

FY 2012 HIGHLIGHTS

We have demonstrated a method for determining the full three-dimensional molecular-frame photoelectron angular distribution in polyatomic molecules using methane as a prototype. Simultaneous double Auger decay and subsequent dissociation allow measurement of the initial momentum vectors of the ionic fragments and the photoelectron in coincidence, allowing full orientation by observing a three-ion decay pathway, (H^+, H^+, CH_2^+). We find the striking result that at low photoelectron energies, the molecule is effectively imaged by the focusing of photoelectrons along bond directions.

We extended this investigation by completing experimental measurements and comparing it to theoretical calculations for the photoionization of CH_4 at the carbon K-edge. Our measurements combined with complex Kohn variational calculations of the photoelectron in the molecular frame reproduce the surprising result that the low-energy photoelectrons effectively image the molecule by emerging along the bond axes. Furthermore, we have observed a dynamic breakdown of axial recoil behavior in one of the dissociation pathways of the intermediate dication, which we interpret using electronic structure calculations.

Ultrafast Holographic X-Ray Imaging and its Application to Picosecond Ultrasonic Wave Dynamics in Bulk Materials

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Principal Investigator:	Rose-Petruck, Christoph
Sr. Investigator(s):	
Students:	0 Postdoctoral Fellow(s), 1 Graduate(s), 1 Undergraduate(s)
Funding:	$140,000

PROGRAM SCOPE

A novel x-ray imaging concept named X-ray Spatial Frequency Heterodyne Imaging (XSFHI) is developed. As the name suggests, the technique relies on the introduction of a “local oscillator” in the spatial frequency space of an x-ray image. Mathematical cross-terms between the local oscillator and the spatial frequency spectrum of the sample, lead to signal enhancements of selectable spatial frequency components that result in image contrast enhancements by orders of magnitude. In contrast to conventional or phase contrast x-ray imaging, a single exposure can be processed to obtain (1) the traditional x-ray absorption image and (2) an image formed exclusively by deflected or scattered x-rays. The signal in the scattered radiation image is depended on, for instance, the size and orientation of nanostructures or phase interfaces in the sample. We have demonstrated that the image contrast is several orders of magnitude larger than that of phase contrast, which itself typically is three orders of magnitude larger than for conventional x-ray absorption imaging. For high emittance x-ray sources or motion blurred samples, the XSFHI makes phase contrast features visible that would otherwise be undetectable. The method does not use any x-ray optics and is well-suited to time resolved imaging studies.

FY 2012 HIGHLIGHTS

Imaging Theory: This year we published the mathematical framework of this imaging concept based on the Kirchhoff-Fresnel integral. We carried out calculations and experiments for x-ray phase contrast imaging showing that the placement of a grating adjacent to the object results in spatial heterodyning of the phase and absorption features of the object. The detected image consists of a conventional absorption and a heterodyned component. The concept is tested by imaging in the soft x-ray regime (water window).

Application to Water Phase Transitions in Carbon Nanotubes: Water in confined spaces can show unusual properties that are not observed in the bulk. 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. Our objective is to develop SFXHI as an x-ray detection method suitable for studying phase transitions in nanomaterials. As the temperature is changed through the phase transition point, the filling of CNTs with water and the expulsion of the water have been observed by our imaging methods. Thus, SFHI can be used to observe macroscopic nanomaterial changes caused by phase transitions.

Electron-Driven Processes in Polyatomic Molecules

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Funding:	$125,000

PROGRAM SCOPE

The focus of this project is the development, extension, and application of accurate, scalable methods for computational studies of low-energy electron-molecule collisions, with emphasis on larger polyatomic molecules that are relevant to the electron-driven chemistry of biological and materials-processing systems. Our approach uses first-principles quantum mechanical calculations to determine the electron-molecule collision cross sections that describe the interactions. For large molecules, such calculations are highly numerically intensive, and efficient use of large-scale parallel computers is therefore essential. Accordingly, our computer codes are highly parallel and scalable, running efficiently on workstation clusters and parallel supercomputers. We have used them to study low-energy electron interactions with various constituents of DNA, including the nucleobases, models of the phosphate and sugar moieties, and larger assemblies, with a view to identifying temporary anion states (resonances) that may be associated with radiation damage to DNA.

FY 2012 HIGHLIGHTS

At present, we are emphasizing studies that couple electron-collision dynamics with nuclear motion in order to map in detail how such temporary anions promote excitation and dissociation of polyatomic molecules.

Collective Coulomb Excitations and Reaction Imaging

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Funding:	$96,000

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 (1) emphasis on reaction imaging while (2) pursuing longtime work on collective Coulomb excitations. As in the past, we continue to place priority on research relevant to experiment.

Electron-Driven Excitation and Dissociation of Molecules

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Funding: $95,000

PROGRAM SCOPE

This program will study how energy is interchanged in electron and photon collisions with molecules leading to excitation and dissociation. In the past, both theory and experiment have been limited in their study of how energy flows in a reaction following electron or photon impact.

Our studies in the area of dissociative attachment will concentrate on the resonant process where there is the capture of the electron into a resonant dissociative state, which then evolves on the excited state (resonant) potential energy surface. The dynamics must be able to describe autoionization since the molecule can re-emit the electron. If no autoionization occurs, the molecule fragments into products, during which the probability may be distributed into various product states due to non-adiabatic coupling.

Our studies of this process follow the comparable treatment of quantum reactive scattering. First we carry out *ab initio* electron scattering calculations at fixed internuclear geometries to determine the resonant energy surfaces and the corresponding surface of autoionization widths, using the Complex Kohn variational method. We then study the dynamics using with the time-dependent wave packet method.

In the case of photon collisions, leading to ionization, especially cases where the photon energy is high, the molecular ion starts in a highly excited initial state. In this case, one must also describe the dynamics of a molecule moving on an excited potential energy surface. In some cases, these surfaces can be autoionizing; but in all cases, there are multiple surfaces that have strong non-adiabatic couplings. Again a combination of electron scattering calculations, bound state quantum chemistry calculations, and dynamics are needed to understand the flow of energy in the system.

We propose to study a number of systems where there is strong coupling between the electronic and heavy-particle degrees of freedom. The theory will use modern *ab initio* techniques, both for the electron scattering and nuclear dynamics, to attempt to understand the flow of energy in the system and to elucidate the mechanisms that underlie this interaction. These include studies of dissociative electron attachment for formic acid and CO_2, highly correlated processes in diatomic photoionization, studying $N_{2,}$ CO and O_2, isomerization of HCCH, leading to snapshots of a chemical reaction and developmental work on ionization of polyatomic molecules at high energies.

Theory and Simulations of Nonlinear X-Ray Spectroscopy of Molecules

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Funding:	$150,000

PROGRAM SCOPE

Theoretical and computational techniques are developed for the description of coherent resonant nonlinear ultrafast x-ray spectroscopies in molecules. New experiments that are made possible by XFEL and HHG sources are proposed. Spectroscopic techniques previously applied in the optical and vibrational regimes are extended to core-excitations at x-ray frequencies. Design principles and tools for multidimensional coherent techniques that make use of the broad bandwidth are presented. Techniques that either study core excitations or use them as triggers for valence electrons with attosecond temporal revolution are proposed. Approximate computational tools that may be applied to large molecules and molecular aggregates are developed. Methods for visualizing electron correlations as revealed by the new measurements are developed.

Basic questions about the dynamics of many electron systems, which are necessary to understand the dynamics of photo-chemically excited states, charge and energy transport are addressed.

FY 2012 HIGHLIGHTS

The two-dimensional stimulated x-ray Raman spectroscopy technique (2D-SXRS), which employs three resonant x-ray pulses, was proposed and shown to probe molecular valence electronic excitations in greater detail than the one-dimensional (two pulse) signal. Signals were calculated for trans-N-methyl acetamide (NMA) with 180as pulses tuned to the oxygen and nitrogen K-edges. Crosspeaks in 2D signals reveal electronic Franck-Condon overlaps between valence orbitals and relaxed orbitals in the presence of the core hole. The signals were found to be sensitive to the order in which the atom-specific x-ray excitations are used to perturb and probe the valence electron configuration. The cross peak pattern and intensities are useful for testing various levels of electronic structure theory.

We showed that broadband x-ray pulses can create wavepackets of valence electrons and holes localized in the vicinity of a selected atom (nitrogen, oxygen, or sulfur in cysteine) by stimulated resonant Raman scattering. The subsequent dynamics reveals highly correlated motions of entangled electrons and hole quasiparticles. This information goes beyond the time-dependent total charge density derived from x-ray diffraction. We showed that 2D-SXRS signals, which depend on a rotationally-averaged sixth-rank tensor, may be simplified by using a Super Magic Angle (SMA) combination of two measurements with specific pulse polarization configurations. Such signals reveal new features not available from the all-parallel polarization configuration.

Electron/Photon Interactions with Atoms/Ions

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Funding:	$80,000

PROGRAM SCOPE

The project's primary objective is to gain a fundamental understanding of the near-threshold electron attachment mechanism and determine accurate electron affinities (EAs) of simple and complex atoms and map the resonance structure in the electron elastic total cross sections. Our novel and elegant Mulholland formula, implemented within the complex angular momentum description of scattering, wherein resonances are rigorously defined as singularities of the S-matrix, is used for the investigations. Regge trajectories allow us to probe electron attachment at its most fundamental level near threshold, thereby uncovering new manifestations and possibilities, as well as determine the reliable EAs of tenuously bound and complicated atomic and molecular systems. Specifically, we use the Regge-pole methodology wherein is embedded the crucial electron-electron correlation effects and the vital core-polarization interaction to (1) obtain accurate near-threshold electron partial and differential cross sections and predict new phenomena, including a fundamental understanding of nanocatalysis through negative ion resonances; (2) investigate low-energy electron scattering from atoms in search of nanocatalysts; (3) study multiple excited negative ion formation in slow electron collisions with complex atoms; (4) explore the role of low-energy electron scattering resonances, including Ramsauer-Townsend minima in nanoscale catalysis; and (5) uncover the physics behind the recently discovered novel self-intersecting Regge trajectories in multi-channel scattering.

Using our new RPAE method implemented within the time-dependent density-functional theory, which can also be used for the study of atoms at off-center position, we also investigate (1) the energy transfer from the C_{60} valence electrons to the photoelectron through the intershell coupling by studying the nature of the newly discovered strong oscillations within the energy range of the C_{60} Giant Resonance exhibited by the absolute differential oscillator strengths for photoabsorption of encapsulated atoms inside a fullerene, and (2) the photoabsorption spectrum of the $A@C_{60}$ endohedral fullerene focusing on the hotly debated dramatic distortion of the Giant Resonances and the suppression effect of the fullerene on confinement resonances. Within the general theory of strongly correlated Fermi systems, the new area of strongly correlated quantum spin liquid is investigated through the dependence of the effective mass on temperature, density, and magnetic field.

FY 2012 HIGHLIGHTS

Our most important accomplishment to date is the discovery of *Novel Mechanism for Nanoscale Catalysis* and linking low-energy electron scattering resonances with chemical reaction dynamics. The ideas have been applied successfully to the oxidation of H_2O to H_2O_2 catalyzed by atomic Au^- and atomic Pd^- ions and to atomic gold negative ion catalysis of methane to methanol without CO_2 emission. These demonstrate clearly the great importance of the knowledge of low-energy electron scattering from atoms, resulting in negative ion formation and the corresponding EAs.

Generation of Bright Soft X-Ray Laser Beams

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Funding:	$145,000

PROGRAM SCOPE

This project 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 motivates the development of more compact and more readily accessible sources of intense soft x-ray laser light for applications. Table-top soft x-ray laser experiments are conducted at Colorado State University to advance the development of gain-saturated, high repetition rate, table-top plasma lasers towards shorter wavelengths. Previously we demonstrate gain-saturated table-top lasers at wavelengths down to λ= 10.9 nm. A goal of this research is to extend gain-saturated table-top lasers to less than 10 nm, demonstrating gain-saturated lasing at a λ= 8.8 nm laser by collisional electron impact excitation of nickel-like lanthanum, and subsequently at increasingly shorter wavelengths by isoelectronic scaling to higher Z ions. The high plasma density at which these short wavelength soft x-ray amplifiers operate is computed to result in collisionally broaden lines that can support the amplification of sub-picosecond soft x-ray laser pulses. According to model simulations, injection-seeding of these amplifiers will allow the generation of extremely intense, fully coherent, sub-picosecond soft x-ray laser pulses on a table top. Ultimately, the size of compact soft x-ray lasers will be further reduced and their average power will be significantly increased using diode pump laser drivers. In this project, we also collaborated in experiments at LCLS that use inner-shell atomic schemes to improve the output characteristics of the x-ray pulses generated at the XFEL by providing wavelength stability and greatly increased monochromaticity.

FY 2012 HIGHLIGHTS

We have observed table-top lasing at wavelengths as short as λ=7.3 nm by isoelectric scaling of collisional excitation soft x-ray lasers to Ni-like Sm. Furthermore, we have realized the first measurement of the time it takes the gain to recover in table-top soft x-ray collisional plasma amplifier that is injection seeded with a short high harmonic pulse. A gain-recovery time of ~ 1.5 ps was measured in an λ= 18.9 nm Ni-like Mo plasma. The results support the possibility of generating ultra-intense fully phase-coherent soft x-ray laser pulses in dense soft x-ray plasma amplifiers. We have also conducted an experiment at LCLS designed to demonstrate stimulated inelastic x-ray Raman scattering. Finally, we have succeeded in increasing the repetition rate of table-top soft x-ray lasers to 100 Hz for the first time, producing a record average power of 0.15 mW at λ=18.9 nm.

Properties of Actinide Ions from Measurements of Rydberg Ion Fine Structure

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Funding:	$130,000

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, U^{6+},U^{5+}. U^{4+}, Th^{4+}, and Th^{3+}, 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 2012 HIGHLIGHTS

The main goal of our program is measurement of properties of Rn-like and Fr-like U and Th ions. Within the past year, we have very nearly met this goal with regard to the Th ions. Optical RESIS studies of Rydberg ions with Rn-like Th^{4+} and Fr-like Th^{3+} cores have been published, giving preliminary determination of some core properties [Phys. Rev. A 82, 022512 (2010); Phys. Rev. A 82, 022512 (2010)]. Much more precise RF studies have now also been completed for both species. A full report of the Th^{4+} results has been published [Phys. Rev. A 83, 062509 (2011); Phys. Rev. A 85, 06452 (2012)], giving precise values of both dipole and quadrupole polarizabilities of this ion. A report of the Th^{3+} results is in preparation. Comparison with theoretical predictions, when available, indicates that only the most advanced relativistic atomic structure methods produce acceptable agreement with these measurements.

Coherent Control of Electron Dynamics

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Funding:	$70,000

PROGRAM SCOPE

The goal of this project is to theoretically analyze electron dynamics as well as the energy exchange between electronic and nuclear dynamics on the natural time scale of the constituents of a molecule interacting with light from a variety of laser sources, including attosecond extreme ultraviolet pulses and ultrashort near-infrared and infrared laser pulses. To this end, we develop theoretical and numerical methods to simulate the response of simple molecules to the laser field over a broad range of wavelengths. We apply our theoretical models to analyze and compare different spectroscopic techniques (strong-field ionization, higher-order harmonic generation, single photon inner and outer shell ionization) proposed for probing structural changes and electron rearrangement in a molecule. Furthermore, we seek for a theoretical understanding of the prospects to control electron dynamics in a molecule with laser light as well as for an identification and interpretation of the dynamics of molecules in the previously rather unexplored infrared wavelength regime. The long-term impact of the project is to meet, on the one hand, the theoretical challenge to understand the coupling between electron and nuclear dynamics beyond the Born-Oppenheimer approximation and, one the other hand, provide theoretical support for the experimental challenge to observe and control molecular dynamics and chemical reactions at the level of electrons.

FY 2012 HIGHLIGHTS

We have successfully analyzed the response of the hydrogen molecular ion to ultrashort intense laser pulses over a broad range of wavelengths. Surprisingly, the results of our numerical simulations show an enhancement of dissociation (over ionization) of the molecule by a few orders-of-magnitude at infrared wavelengths. This finding is in contrast to a long standing assumption that one cannot induce vibrational excitation and dissociation of a molecule with a strong laser pulse without ionizing the molecule. The basis of our theoretical predictions is an efficient coupling between different vibrational states of the molecule via two- and higher-order photon transitions. Currently, we analyze recent experimental observations of substantial time delays during photoionization from different sub-shells.

Molecular Dynamics Probed by Coherent Electron and X-rays

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PROGRAM SCOPE

The goal of this work is to develop novel ultrafast probes of coupled dynamics in molecules and nanosystems. This is a very exciting time for ultrafast x-ray science, with new and unique large- and small-scale sources now available. Our recent research in tabletop coherent x-ray sources dramatically expanded the photon energy range over which bright femtosecond-to-attosecond high harmonic (HHG) beams can be generated. Using a tabletop mid-infrared femtosecond laser to drive the HHG process, bright HHG beams emerge as a soft x-ray supercontinuum, that spans from the UV to the keV regions of the spectrum (to below 8 Å), with sufficient flux for application experiments. Ultrafast x-rays, by virtue of their short wavelength, are ideal as a probe of the fastest dynamics in matter at the nanoscale. Using elemental absorption edges, site-specific chemical dynamics can be captured. Coupled with advanced theory, this new capability makes it possible to follow the coupled charge/spin/phonon motions that dynamically rearrange during charge transfer, phase change, or chemical reactions. This work is relevant to understanding matter in excited and highly-excited regimes, where the Born-Oppenheimer picture can break down and non-adiabatic processes dominate. This project also seeks to understand the response of matter to strong laser fields, in particular mid-infrared (mid-IR) femtosecond laser fields, in order to develop new probes of structural and orbital dynamics in nanoscale systems.

FY 2012 HIGHLIGHTS

We have two major highlights from 2012. First, we showed that when an atom is irradiated by an intense mid-infrared femtosecond laser pulse, the simple picture used to describe how an atom ionizes needs to be extended to include the fact that the electron can re-encounter the parent ion multiple times before finally escaping. Second, we discovered that we can use laser pulses to control the explosion of highly-excited triatomic molecules. After N_2O is irradiated by a burst of x-rays, the molecule breaks apart through a competition between dissociation and ionization of a second electron. In the presence of an intense femtosecond laser field, breaking the N-O bond can be preferentially enhanced over breaking the N-N bond, indicating the presence of laser-induced non-adiabatic electron motion.

Optical Multi-Dimensional Spectroscopy of Semiconductor Quantum Dots

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Funding:	$120,000

PROGRAM SCOPE

Multidimensional Fourier transform spectroscopy techniques in the infrared and optical domains have been developed in the last decade. Multidimensional Fourier transform spectroscopy originated in NMR, where it disentangled congested spectra and revealed coupling of the underlying resonances. In the infrared, it is now being routinely used to probe molecular vibrations. In the near-infrared and visible regimes, it is being used to study electronic transitions in molecules. Under DOE support, we are using two-dimensional Fourier transform spectroscopy to study electronic excitations, mainly excitons, in semiconductor nanostructures. In earlier phases of this project, we studied excitons in GaAs quantum wells and, more recently, GaAs natural quantum dots that form in thin quantum wells. Currently, we are focusing on studying InAs self-organized quantum dots grown by molecular beam epitaxy.

FY 2012 HIGHLIGHTS

We obtained our first two-dimensional Fourier transform spectra of InAs self-organized quantum dots. The spectra show off-diagonal peaks due to biexcitons. An upper cross peak is attributed to fifth-order optical nonlinearities, whereas the lower cross peak is due to the customary third-order signal. Using polarization can suppress the signal due to excitons, revealing the biexciton signal as well as signals due to trions resulting from unintentional doping. Analysis of the biexciton peak reveals that the biexciton binding energy does not vary with dot size and the biexciton energy is strongly correlated with the exciton energy. Both of these results differ from conclusions derived from single dots studies, although in those, there are other effects that could cause fluctuations and it is hard to accumulate good statistics. In addition, by using an alternate projection of the two-dimensional spectrum, it is possible to measure the fine-structure splitting due to dot anisotropy.

Physics of Correlated Systems

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Funding:	$145,000

PROGRAM SCOPE

This theoretical research effort tackles problems at the cusp of the field’s current abilities to describe correlated system governed by quantum mechanics, primarily in the context of atoms and molecules, in some cases interacting with external static or time-dependent fields. A standard approach in atomic and molecular physics is to treat the electrons approximately, as though they are moving independently of one another or independently of other degrees of freedom, such as the internuclear vibrations and rotations or an external field. While such uncorrelated approximations are effective in a number of situations, there are many phenomena that require more sophisticated treatments of the quantum behavior. It has been a longstanding goal of the research community to develop theoretical techniques capable of describing such nonperturbative correlations, and this project has been engaged in this class of endeavors. The current research group has been studying the effects of a dressing laser field on electron collisions and half-collisions, the latter representing photoionization processes. In addition, studies have continued in the area of electron collisions with a molecular ion that triggers dissociation and vibrational excitation, especially the process of dissociative recombination (DR), which is one of the most fundamental reactive chemical processes yet one of the most difficult for theory to handle. This overview will focus primarily on work performed and papers published during the past year, with some discussion of future directions.

FY 2012 HIGHLIGHTS

A novel direction in atomic, molecular, and optical physics was triggered by the ability to combine an ultrafast infrared laser pulse with XUV light spawned by a high harmonic generation process. A particularly noteworthy experiment, published a few years ago by the group of Stephen Leone [Chem. Phys. 350, 7 (2008)], demonstrated how a transient absorption experiment could yield control to some extent over the absorption of XUV light by helium in the photon energy range near 60 eV. While a phenomenological treatment did a reasonable job of accounting for those experimental results in the language of few-level quantum optics, we tested theory by developing techniques that could directly solve the time-dependent Schroedinger equation for this simplest two-electron atom. This project was able to build on our previous extensive solutions of the time-independent Schroedinger equation for two-electron atoms, but implementing time-dependent propagators on top of that machinery required extensive retooling and experimentation with alternative algorithms. Our calculations published this year have successfully described the complicated transient absorption spectra observed experimentally for pump-probe time delays of 0, 20 fs, 40 fs, 60 fs, and 80 fs.

Reactive Scattering of Ultracold Molecules

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PROGRAM SCOPE

In an effort to probe ever deeper into the fundamental dynamics of chemical reactions, one is faced these days with two options. One may either increase resolution in the time domain and deliberately push around molecular constituents, as in the rapidly maturing field of ultrafast dynamics, or increase resolution in the energy domain by effectively slowing the beams, as is done in the nascent field of cold and ultracold molecules. This program is concerned with the latter approach. It seeks to address what new information may be afforded by molecular gases cooled to sub-milliKelvin temperatures. In these experiments, the incident channel of the reactants can be completely specified in terms of the internal state, as well as an extremely low relative translational energy that, in favorable cases, allows probing the reactivity of a single partial wave in the incident channel.

FY 2012 HIGHLIGHTS

We have considered problems relevant to both the long-range and short-range physics. For the long-range, we seek to exploit the value of multichannel quantum defect theory (MQDT) for not only calculating accurate results, but also parametrizing complex scattering observables such as resonances in a compact way. MQDT is known to be a powerful method when applied to ultracold collisions of atoms. It has always been problematic, however, when applied to molecules, where rotational excitation and intrinsically anisotropic potentials can make high partial waves relevant. In collaboration with C. Greene, we have recently perfected a method for generating numerically accurate, linearly independent QDT basis functions for this purpose, opening up MQDT as a powerful tool for molecular cold collisions.

In a second project, we have explored the role of scattering resonances in realistic molecules. Here we have focused on ground-state alkali dimers, which have been successfully created at ultracold temperatures in several labs (although so far only one has observed them colliding). We have estimated the density of ro-vibrational resonant states for these systems, finding them to be huge. In such a situation, it is probably hopeless to identify each resonance explicitly. Rather, it is more reasonable to understand the *statistical* consequences of these many resonances. To this end, we have constructed a hybrid theory, which combines random matrix theory from nuclear physics to assess the distribution of resonant states and their width, with the MQDT that provides complete detail of such matters as field and energy dependence near threshold.

New Scientific Frontiers with Ultracold Molecules

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PROGRAM SCOPE

On the experimental front cold polar molecules (OH and YO molecules), we have recently achieved two major breakthroughs. The first is the observation of direct evaporative cooling of OH molecules in a magnetic trap. The second is the implementation of the first magneto-optic trap (1D and 2D) for YO. OH molecules are prepared by Stark deceleration followed by loading in a permanent magnetic trap, resulting in a Boltzman distribution with a 60 mK temperature. We first observed two-body collisions. When we implemented forced evaporation by using a radio frequency knife to selectively remove relatively hot molecules, we observed more than a factor of 10 decrease in the sample temperature, with a corresponding increase in the phase space density by 100. This research direction is extremely exciting, as we expect to be able to further cool the molecules to a much lower temperature. On the other front, extending the magneto-optical trapping technique to diatomic molecules promises to be a general method for the creation of ultracold systems with new, complex interactions. We have demonstrated one- and two-dimensional transverse laser cooling and magneto-optical trapping of the diatomic molecule yttrium monoxide (YO). A quasi-closed cycling transition allows us to scatter >1000 photons, resulting in one-dimensional Doppler cooling of a YO molecular beam from a temperature 25 mK to 5 mK. With the addition of a quadrupole magnetic field, we observe additional cooling of the YO beam due to a magneto-optical restoring force and achieve temperatures as low as 3 mK.

FY 2012 HIGHLIGHTS

Building on the previous success of producing a rovibronic ground-state molecular quantum gas in a single hyperfine state, we have realized long-lived ground-state polar molecules in a 3D optical lattice, with a lifetime of up to 25 s, which is limited only by off-resonant scattering of the trapping light. Starting from a 2D optical lattice, we observe that the lifetime increases dramatically as a small lattice potential is added along the tube-shaped lattice traps. The 3D optical lattice also dramatically increases the lifetime for weakly bound Feshbach molecules. For a pure gas of Feshbach molecules, we observe a lifetime of greater than 20 s in a 3D optical lattice; this represents a 100-fold improvement over previous results. This lifetime is also limited by off-resonant scattering, the rate of which is related to the size of the Feshbach molecule. Individually trapped Feshbach molecules in the 3D lattice can be converted to pairs of K and Rb atoms and back with nearly 100% efficiency.

Experiments in Ultracold Collisions and Ultracold Molecules

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PROGRAM SCOPE

This project is focused on producing molecules at sub-millikelvin temperatures via the process of photoassociation. Beginning with ultracold Rb atoms in a magneto-optical trap, we use pulses of frequency-chirped light to form excited-state molecules by long-range photoassociation of colliding atoms. These excited molecules then undergo radiative decay into the ground state, typically populating high vibrational levels. Nanosecond timescale manipulations of the frequency and amplitude of the pulses allow coherent control of the molecular formation process. To detect the resulting ground-state molecules, we employ resonantly-enhanced multiphoton ionization with a pulsed dye laser, followed by time-of-flight mass spectroscopy.

In parallel with the molecular experiments, we are developing the technology to enable production of pulses and frequency chirps on subnanosecond time scales. Starting with single-frequency light from a diode laser, we use fiber-optic-based electro-optical phase and intensity modulators to produce chirps and pulse shapes, respectively. Both modulators are driven by a fast arbitrary waveform generator in order to generate the desired chirped pulses. The output is then amplified by a tapered semiconductor amplifier or by injection locking a slave diode laser. Heterodyne analysis is the main tool for diagnosing the output pulses.

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 2012 HIGHLIGHTS

We have recently used pulses of frequency-chirped light to produce ground-state $^{87}Rb_2$ molecules and found a dramatic difference in the production rate for positive and negative chirps. Using quantum simulations of the molecule formation process, we have identified a mechanism for this difference. The positive chirp produces excited molecules and then transfers them, by stimulated emission, to a weakly bound level of the ground state. This cannot happen for the negative chirp because the two steps, absorption and stimulated emission, would occur out of order. As a next step, we will produce chirps on faster time scales and increase the intensity of the chirped pulses in order to enhance these coherent effects.

Formation of Ultracold Molecules

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Sr. Investigator(s):	
Students:	1 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$102,000

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). These findings are essential to the growing field of ultracold chemistry and its control.

FY 2012 HIGHLIGHTS

We have made progress on the four main axes of research listed below.

(1) Rydberg-Rydberg interactions: We investigated the existence of potential wells of doubly-excited Rb atoms due to l-mixing. We found deep wells for certain symmetries and obtained their n-scaling of the equilibrium depth and separation. We also studied how to produce them using photo-association.

(2) Potential Energy Surfaces (PES) and reactions: We obtained accurate *ab initio* PES for the ground state of a trimer (Li_3) and its three-body molecular van der Waals coefficients. We also studied the collisions of trapped molecules with slow beams, particularly of OH with ^{4}He, and computed rate coefficients for reaction and vibrational quenching of the ultracold collision $D+H_2(v,j=0)$ for a wide range of initial vibrationally excited states v, and found two distinct regimes: for $0 \leq v \leq 4$ (barrier dominated) and for $v \geq 5$ (barrierless). We computed the structure of all alkali tetramers formed from $X_2+X_2 \rightarrow X_4$, $X_2+Y_2 \rightarrow X_2Y_2$, and $XY+XY \rightarrow X_2Y_2$ association reactions, found two stable structures [rhombic (D_{2h}) and planar (C_s)], and found barrierless pathways for those reactions. We computed properties of molecular ions (Be_2^+ and Ca_2^+) and found double wells correlated to ground state atom+ion.

(3) Long-range interaction between diatomic molecules: Although we found the minimum energy path for the reaction KRb+KRb$\rightarrow$$K_2$+$Rb_2$ to be barrierless, we showed that long-range barriers originating from anisotropic interactions (e.g., quadrupolar) could exist and be controlled by external electric fields.

(4) Formation of dimers and tetramers: We have started to explore how our previous work on FOPA (Fehsbach Resonance Photo-Association) could enhance pump-dump schemes to produce ground state molecules. We also started the same approach to form ultracold tetramers. In fact, by controlling the long-range interaction between polar diatomic molecules using external DC electric field, we could increase the formation rate of tetramers.

In the next period, we will extend our Rydberg calculations to long-range macrotrimers made of three Rydberg atoms. We will compute electronic properties of molecules (PES and moments), especially for the molecular ions, where not much is available. Finally, we plan to work on long-range interactions between molecules in more complex systems (e.g., diatomic + triatomic molecules, etc.).

Algorithms for X-Ray Imaging of Single Particles

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Funding: $150,000

PROGRAM SCOPE

The many-orders-of-magnitude gains in x-ray brightness recently achieved by free-electron laser sources such as the Linac Coherent Light Source (LCLS) are driving a fundamental review of the data analysis methods in x-ray science. It is not just a question of doing the old things faster and with greater precision, but doing things that previously would have been considered impossible. My group at Cornell is working closely with experimental groups at LCLS to develop data analysis tools that exploit the full range of opportunities made possible by the new light sources.

FY 2012 HIGHLIGHTS

The work that has attracted the most attention in the past year is the demonstration of algorithmic image reconstruction from ultra low flux x-ray data. Motivated by the urgent need to check the high quantum efficiency of Cornell's Pixel Array Detector (PAD) for the LCLS, the design of the experiment is surprisingly simple. A table-top x-ray source, highly attenuated by a lead sheet, is directed at a single module of the PAD. In front of the detector there is a mask, a complex shape cut out of another lead sheet, that is mounted on a stage that can be rotated about the beam axis. The beam attenuation went as far as giving an average of only 2.5 photons recorded on the detector per exposure.

The quantum efficiency of the PAD could have been demonstrated by collecting statistics in these ultra-low flux conditions. However, to bring the experiment closer to the single-particle imaging setting, we gave the mask a random rotation between each exposure (mimicking the randomness of particle orientations). We collected nearly a half-million exposures, each recording very few photons and without knowledge of the mask rotation at the time of the exposure. Despite these adverse experimental conditions, our expectation maximization algorithm had no trouble reconstructing the shape of the mask.

Ionization of Free and Confined Atoms and Ions

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Funding:	$70,000

PROGRAM SCOPE

The goals of this research program are to (1) provide a theoretical adjunct to, and collaboration with, the various atomic and molecular experimental programs that employ latest generation light sources, particularly ALS, APS, and LCLS; (2) generally enhance our understanding of the photoabsorption process; and (3) study the properties (especially photoabsorption) of confined atoms and ions. To these ends, calculations are performed employing and enhancing cutting-edge methodologies to provide deeper insight into the physics of the experimental results, provide guidance for future experimental investigations, and seek out new phenomenology, especially in the realm of confined systems. The main areas of programmatic focus are (1) manifestations of nondipole effects in photoionization, (2) photodetachment of inner and outer shells of atoms and atomic ions (positive and negative), and (3) studies of atoms endrohedrally confined in buckyballs, C_{60}, particularly dynamical properties. Flexibility is maintained to respond to opportunities.

FY 2012 HIGHLIGHTS

Among the more important results obtained this year, we have understood many of the effects of confinement of alkali earth atoms sequestered inside C_{60} molecules, including hybridization of the atomic orbitals, coupling between photoionization channels of the atom and the plasmons of the confining shell, and the confinement resonances or oscillations induced by the geometry of the confinement. We have also succeeded in extending the R-Matrix formalism to include the effects of confinement on a trapped atom and performed a calculation on Xe 4d, which showed excellent agreement with the experiment.

For free atoms/ions, we have extended our previous studies of the 19-electron ions to the photoionization of the lowest three states of Ca^+ to further trace out the behavior of the giant dipole resonances that were found in higher-Z members of the sequence. The Ca^+ results were found to be in excellent agreement with the experiment. In addition, in looking at inner-shell photoabsorption by Fe^{14+}, which is of importance in both laboratory and astrophysical plasmas, we have introduced both Radiative and Auger damping. Including both of these effects gives excellent agreement with experimental photoionization results and highlights the difference between photoabsorption and photoionization for x-ray-induced inner-shell ionization of atoms and ions.

Novel Nanoplasmonics Theory: Energy Transformation Processes at the Nanoscale in Ultrafast and Strong Laser Fields

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Funding: $100,000

PROGRAM SCOPE

The program is aimed at fundamental theoretical investigations of a wide range of phenomena where quantum properties of matter and surface plasmon excitations are of primary importance. Among phenomena where quantum behavior of surface plasmons defines their fundamental physics is spaser (quantum generation and amplification of nanoscopic optical fields). A example of such a phenomenon is the recently predicted effect of metallization of dielectrics [Phys. Rev. Lett. 107, 0866021-5 (2011)] or spaser [Phil. Trans. R. Soc. A 369, 3510-3524 (2011)]. Matter in ultrastrong and ultrafast optical fields is another research field of this Program where quantum phenomena play a dominating role [Nat. Phot. 5, 677-681 (2011); Phys. Lett. 100, 051904-4 (2012)]. Overall during this grant period, the grant provided a major support that resulted in publications of Refs. [Phys. Rev. Lett. 107, 0866021-5 (2011); Phil. Trans. R. Soc. A 369, 3510-3524 (2011); Nat. Phot. 5, 677-681 (2011); Appl. Phys. Lett. 100, 051904-4 (2012); Opt. Express 19, 22029-22106 (2011); Nature, (In Print) (2012)].

FY 2012 HIGHLIGHTS

We have investigated, both theoretically and experimentally, attosecond electronic process in a dielectric solid induced by ultrastrong and ultrafast laser pulses [6]. Subfemtosecond solid-state spectroscopy of the underlying electron processes reveals the feasibility of manipulating the electronic structure and electric polarizability of a dielectric with the electric field of few-cycle near-infrared (NIR) light. We irradiate a dielectric (fused silica) with a waveform-controlled NIR several-V/Å few-cycle light pulse and probe changes in extreme ultraviolet (XUV) absorptivity and NIR reflectivity on a sub-femtosecond to few-femtosecond time scale. The field-induced changes follow, in a highly nonlinear fashion, the turn-on and turn-off behavior of the driving field, in agreement with the predictions of a quantum mechanical theory. The ultrafast reversibility of the effects implies that physical properties of a dielectric can be controlled with the electric field of light, offering the potential for petahertz-bandwidth signal manipulation.

Ultracold Sodium and Rubidium Mixtures: Collisions, Interactions and Heteronuclear Molecule Formation

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Sr. Investigator(s):	
Students:	1 Postdoctoral Fellow(s), 0 Graduate(s), 2 Undergraduate(s)
Funding:	$140,000

PROGRAM SCOPE

This program centers on quantum gases of ^{23}Na and ^{87}Rb, with the goal of observing collisions and interactions in binary mixtures. In the current period, our research has focused on single species interactions and dynamics with a ^{23}Na Bose-Einstein condensate.

FY 2012 HIGHLIGHTS

We have recently begun to explore the correspondence between a spinor Bose-Einstein condensate of sodium atoms and a quantum-mechanical rotor. Spinor BECs can offer unique insights into field-induced alignment in diatomic molecules. The role of the external aligning field is played by an external magnetic field through the quadratic Zeeman effect. Molecular rotation corresponds to rotations in spin space induced purely by interactions between atoms. For sodium atoms, with total hyperfine spin $F = 1$, the spin-dependent interactions are anti-ferromagnetic, leading to a nematic order parameter where spin alignment rather than orientation is the relevant degree of freedom. Thus a sodium BEC corresponds particularly closely to a homonuclear diatomic molecule. The moment of inertia is macroscopic in size, and therefore is very easily aligned by weak magnetic fields in the range of 0.1-1 Gauss. However, unlike a heavy diatomic, thermally occupied rotations are negligible; and the spinor BEC is very close to its energy ground state. Thus it offers insights into field induced alignment and wavepacket dynamics in a regime typically not easily accessed in other systems.

We observed the dynamics of the spinor BEC consisting of a pure $m=0$ spin projection as it was rapidly tuned from positive to negative quadratic energy shift q. The value $q = 0$ constitutes a quantum critical point. Negative q was realized using the AC Stark shift from a far-off resonance microwave field. By spatially imaging the 3 spin components of a sodium BEC, we observed a rapid dispersion of the initially localized wavepacket associated with the formation of pairs of atoms with spin projection +/- 1. These pairs appeared through a dynamical instability associated with the quantum phase transition as localized spin domains that grew in size, exhibiting coarsening dynamics.

Future work on spinor BEC will explore the correspondence more closely, including the possibility to observe wavepacket revivals and other nonclassical signatures of rotor dynamics.

Low-Energy Electron Interactions with Liquid Interfaces and Complex Biological Targets

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Funding:	$145,000

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 (25-200 eV) 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 interatomic and intermolecular Coulomb decay and energy exchange via localized shape and Feshbach resonances in the non-thermal damage of biological interfaces. The targets we will examine range in complexity from defined molecular thin films of biologically relevant biomolecules (nucleotides, amino acids, DNA, and RNA), aqueous solution interfaces, and epitaxial graphene.

FY 2012 HIGHLIGHTS

Low-energy electron scattering was used as a tool to induce damage to double stranded (DS) DNA and single stranded (SS) DNA films. The films were deposited either on a gold evaporated Si-substrate or on a Chemical Vapor Deposition grown graphene monolayer supported by a gold evaporated Si-substrate. The DNA film damage was analyzed using Raman scattering micro-spectroscopy. The Raman spectra reveal significant damage at very low-energies with most single strand breaks (SSBs) occurring below 1eV. Double strain breaks (DSBs) do not occur until above 5eV. A new platform such as graphene was used for the enhancement of the DNA signature Raman peaks. This approach has a better signal/noise ratio which allows more accurate molecule specific assessment of the damage. The present results indicate that the damage involves low-lying shape resonances and compound Feshbach resonances initially located on the bases. The electron is then transferred to the sugar-phosphate region, and damage occurs primarily due to occupancy of the dissociative σ levels.

Ultracold Molecules: Physics in the Quantum Regime

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Sr. Investigator(s):	
Students:	1 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding:	$140,000

PROGRAM SCOPE

Our research encompasses a unified approach to the trapping of diverse chemical species of both atoms and molecules and the study of their collisions. We have developed lasers and apparatus for trapping both CaH and CaF molecules. This includes high power lasers at all necessary wavelengths. Our current goal is to magnetically trap CaH or CaF. This will be done by taking molecules from our newly developed slow beam source, with velocity of about 50 m/s, and optically pumping them into a deep magnetic trap. All apparatus is now in place, and we are planning our cooled down for the first time in October 2012. We have also constructed and tested a smaller, auxiliary apparatus for production of CaF beams and optical pumping tests. We are also, in tandem, working on cooling and spectroscopy of large molecules. We have now demonstrated a full method for trace detection with high specificity of small organic molecules in a mixture.

Our immediate plans are to optically pump molecules in the trapping region. We are also now performing CaF beam and optical pumping studies in our smaller, auxiliary apparatus. We are also planning on introducing mixtures into our large molecule cooling apparatus for demonstration of trace detection.

FY 2012 HIGHLIGHTS

Publications from this period are:

(1) Buffer Gas Cooling and Intense, Cold, Slow Molecular Beams, N. R. Hutzler, Hsin-I Lu, J. M. Doyle, *Chemical Reviews Special Issue on Ultracold Molecules*, accepted published electronically 9 May 2012 10.1021/cr200362u (2012).

(2) Cooling molecules in a cell for FTMW spectroscopy, D. Patterson and J. M. Doyle, *Molecular Physics*, accepted (2012).

Structure and Dynamics of Atoms, Ions, Molecules, and Surfaces

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Students:	5 Postdoctoral Fellow(s), 20 Graduate(s), 5 Undergraduate(s)
Funding:	$2,500,000

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, the MARS laser, and the newly-installed 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 attosecond 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 2012 HIGHLIGHTS

The lab has seen many upgrades during this year. One of the more significant is the addition of a world-class 10 kHz ultrafast intense laser system funded by a DOE equipment grant. PULSAR, which was recently delivered and installed by KMLabs, is rapidly being incorporated into our research. Another change includes new and upgraded environments provided by the university in anticipation of new laser systems.

We have been involved in a variety of projects this past year. Some of the most significant are: imaging ultrafast molecular dynamics with laser-induced electron diffraction, attosecond tracing of correlated electron-emission in non-sequential double ionization, attosecond control of orbital parity mix interferences and the relative phase of even and odd harmonics in an attosecond pulse train, and enhancing the intense field control of molecular fragmentation.

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

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Funding:	$169,000

PROGRAM SCOPE

The major thrust of this project is to provide the theoretical foundation for probing the time-dependent structural change of a transient molecule using existing few-cycle femtosecond infrared lasers. Currently there are no established tools for imaging the evolution of the chemical and biological transformations of a molecule with temporal resolution of a few femtoseconds. When a molecule is exposed to an infrared laser, electrons that were released in the early phase of the laser field can be driven back by the laser to recollide with the parent molecular ion. The recollisions of these returning electrons with the parent ions reveal the structure information of the target, with the temporal resolution set by the pulse duration of the laser. If the returning electrons are elastically scattered, the resulting high-energy photoelectron momentum distributions can be used to extract the elastic scattering differential cross sections (DCS). The DCS can be analyzed to reveal the positions of atoms in the molecule. Similarly, if the returning electrons recombine with the parent ion and emit high-order harmonics (HH), the retrieved photo-recombination cross sections reveal the bonding of outer-shell electrons. For a dynamic system, the DCS and the HH spectra can be used to probe the transient structure of the molecules under investigation.

FY 2012 HIGHLIGHTS

In the last year, the validity of our theoretical modeling has been established. From the photoelectron spectra, the bond length of a diatomic molecule has been extracted. For N_2, the retrieved bond length is consistent with the known bond length of the neutral N_2. For O_2, the retrieved bond length was 0.1 ^{o}A shorter. The latter was interpreted as due to the shrinking of the interatomic distance when an electron is removed from the molecule. This result was published in April 2012, in Nature. Using HH spectra, we further established that experimental spectra can now be compared directly to theoretical calculations, and the analysis of the data reveals the structure information of the molecules.

Atomic and Molecular Physics in Strong Fields

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Funding: $105,000

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. For the new theoretical methods, we are developing the generalized Floquet formalisms as well as the self-interaction-free time-dependent density functional theory (TDDFT) for the nonperturbative treatment of strong-field AMO processes. For the new computational methods, we are developing the time-dependent generalized pseudospectral (TDGPS) methods in different coordinate systems for accurate and efficient numerical solution of time-dependent Schrödinger equation (TDSE) and time-dependent Kohn-Sham (TDKS) equation in space and time. 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 diatomic and small polyatomic molecules, time-frequency spectrum, coherent control of HHG processes for the development of tabletop x-ray laser light sources, and for the exploration of attosecond AMO processes, etc.

FY 2012 HIGHLIGHTS

We have made several significant advancements in FY 2012: (1) We report a new mechanism and experimentally realizable approach for the coherent control of the generation of an isolated and ultrashort attosecond (*as*) laser pulse from atoms by means of the optimization of the two-color and three-color laser fields with proper time delays. (2) We have developed a new TDGPS method in the momentum space for high-precision solution of TDSE and its application to the study of multi-photon above-threshold ionization (ATI) in super-intense high-frequency free-electron laser fields. (3) We have performed an *ab initio* theoretical analysis and precision calculation to explore the quantum origin of the low-energy structure (LES) observed in the recent experiments. Our study shows that an important role in the shaping of LES is played by the effect of Coulomb attraction in the final electron state and the Coulomb threshold effect. (4) We present a TDDFT approach with proper asymptotic long-range potential for accurate nonperturbative treatment of multiphoton ionization and HHG of both homonuclear and heteronuclear diatomic molecules with arbitrary orientation in intense laser pulses.

Molecular Photoionization Studies of Nucleobases and Correlated Systems

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Funding:	$155,000

PROGRAM SCOPE

Our research involves molecular photoionization studies that allow us to probe correlated events in fundamental scattering phenomena, and our joint theoretical-experimental program provides a window into the microscopic aspects that are of central importance in AMO and chemical physics generally. Moreover, this photoionization research is central to the mission of the Department of Energy across a wide swath of pivotal topics, including but not limited to ultrafast dynamics, high harmonic generation, and probes of nonadiabatic processes, such as surface hopping at conical intersections. We have the experimental and theoretical tools to generate detailed and unambiguous data on the scattering dynamics. The unifying theme is that correlations between electron scattering dynamics and molecular geometry highlight inherently molecular aspects of the photoelectron behavior, and we investigate the sensitivity of the photoelectron half-scattering to molecular geometry via vibrationally-resolved measurements over broad ranges of scattering energy. The experimental strategy is two-fold: (1) exploit high-resolution photoelectron spectroscopy at the Advanced Light Source, i.e., maintaining the high-resolution in the electron channel over a wide range of incident photon energies, and (2) studying high harmonic generation using ultrafast laser systems at the DOE McDonald Lab at Kansas State University (in collaboration with Prof. Carlos Trallero). In addition to the experiments, we have a rigorous theoretical component to all of this research supervised by Prof. Robert Lucchese at Texas A&M University; the theoretical efforts employ Schwinger variational scattering calculations, which provides a rigorous *ab initio* approach that is computationally tractable and physically realistic. The methods used for the proposed work have been applied to a variety of systems in our previously funded research, so the feasibility of the proposed research has been clearly demonstrated. Collectively, this work provides a window on complex systems and correlated phenomena that lie at the nexus of the Department of Energy's grand challenges.

FY 2012 HIGHLIGHTS

A major component of our recent work has been to develop connections between molecular high harmonic generation and photoionization dynamics. The two phenomena are intimately connected because a central aspect of high harmonic generation involves the high-field driven electron inelastically traversing the molecular framework. This is the conjugate process to photoionization. We have performed experiments on a series of molecules, including SF_6, $SiCl_4$, and CF_4. This work is done collaboratively with Kansas State researchers, primarily Profs. Carlos Trallero and C.D. Lin. In the case of SF_6, we have observed a pronounced dip at the 17th harmonic. This energy corresponds closely to a shape resonance in the photoionization continuum. We have seen similar, albeit less dramatic effects, in the other molecules studied. In addition, we have completed photoelectron work on a number of complex polyatomic systems, including acrolein and cytosine.

Condensed Matter Spectroscopy on Ultrafast Time Scales and Mesoscopic Length Scales

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Funding:	$200,000

PROGRAM SCOPE

Understanding energy flow in nanostructures is very challenging because the basic models describing ballistic and quasi-ballistic transport are still under development, particularly in two and three dimensions. Thermal energy is carried by phonons that travel ballistically away from a nanoscale heat source for a significant distance before experiencing collisions, leading to a non-local (i.e., non-diffusive) thermal energy distributions. However, despite considerable theoretical discussions and direct application to thermal management in nanoelectronics, nano-enabled energy systems, and nanomedicine, until recently this non-diffusive heat dissipation had not been experimentally observed to date, even for simple one-dimensional structures. Using coherent short wavelength x-ray beams to probe at the nanoscale (<< 100 nm), we are exploring energy flow from 1 – 3D nanostructures both theoretically and experimentally, to uncover a general understanding of how energy moves through nanoscale interfaces. This work also has important implications for probing the elastic properties of materials at the physical limits (< 10 nm). With coherent x-ray beams, we can probe optically excited nanostructures to observe surface acoustic waves and thermal transport on nanometer length scales. In complementary optical measurements, we can generate bulk compressional and shear acoustic waves and further study short-wavelength, high-frequency (GHz-THz range) elasticity and energy flow through nanostructured materials.

FY 2012 HIGHLIGHTS

We explored heat flow in 2D nanostructures and observed strong effects of confinement of energy-carrying phonons in small 2D elements and of ballistic, non-diffusive thermal transport kinetics on nanometer length scales. A 3D thermal transport model is needed to treat heat migration from an array of 2D metallic squares into a bulk substrate, and a finite element simulation framework is under development to fully describe our results. We recorded the shortest-wavelength surface acoustic waves observed to date (45 nm wavelength). We completed an extensive study of GHz-frequency acoustic waves in glass-forming liquids that revealed high-frequency structural relaxation dynamics, and we demonstrated optical generation and detection of THz-frequency acoustic waves in semiconductor superlattice structures as well as convenient optical detection of THz-frequency acoustic waves. We are developing versatile platforms for measurement of thermal transport and acoustic properties on nanometer length scales that will be applicable to a wide range of materials and structures.

Understanding and Controlling Strong-Field Laser Interactions with Polyatomic Molecules

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Funding:	$75,000

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.

FY 2012 HIGHLIGHTS

We developed a new method to explore electronic coherence that involves pairs of replica ultrafast pulses. The method can be used with ultrashort pulses at any wavelength and can be applied to study dynamics in gas, liquid, solid, and plasma states of matter. We have made direct measurements of the extent of electronic coherence during strong-field excitation of polyatomic molecules. Measurements on DCPD have uncovered the first evidence of long-lived electronic coherence during strong field laser-polyatomic molecule interactions. This will lead to two publications, one on the observation and a second one exclusively on coherent control.

Experiments on IR-144 dissolved in methanol have led to detailed understanding of the early optical response of large organic molecules in solution, including the solvation Stokes shift. Our results have been confirmed through additional experiments as a function of temperature and molecular structure. Further studies on IR 144 by exploiting the Phase and Amplitude Shaping have also been carried out to study the mechanism of decoherence in solution, and a manuscript reporting the results is currently in preparation. Additional experiments using chirped pulses have led to a new theoretical model to interpret the early solvation dynamics. These results complete some of the earliest results in the field of laser control using chirped pulses. In particular, we found that the magnitude of the chirp effect on fluorescence intensity and stimulated emission is a second order process on laser intensity; but the shape of the chirp dependence is independent of laser intensity.

Dynamics of Few-Body Atomic Processes

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Students: 1 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding: $120,000

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, for example, 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 2012 HIGHLIGHTS

We have derived quantum-mechanically an analytic result for the above-threshold (multi-photon) ionization (ATI) probability of an atom for a short (few-cycle) laser pulse of any shape and duration that is valid at the high-energy end of the well-known ATI spectrum plateau. These analytic results allow one to describe very accurately the left-right asymmetry as well as the large-scale (intracycle) and fine-scale (intercycle) oscillations in ATI spectra. Agreement with results of accurate numerical solutions of the time-dependent Schrödinger equation is excellent.

By solving the two-active-electron, time-dependent Schrödinger equation in its full dimensionality, we have also investigated the carrier-envelope-phase (CEP) dependence of single ionization of He to the $He^+(1s)$ state triggered by an intense few-cycle attosecond pulse. Asymmetries are found in the differential probability for ionization of electrons parallel and antiparallel to the linear polarization axis of the few-cycle attosecond laser pulse. We find a large enhancement of this asymmetry in the vicinity of two-electron doubly-excited (autoionizing) states on an energy scale comparable to the widths of the autoionizing states. Recent extensions of our calculations to intense few-cycle attosecond pulse ionization plus excitation of He to $He^+(n=2)$ show enormous asymmetries and opposite behaviors for leaving the ion in the $He^+(2s)$ and $He^+(2p)$ states.

Finally, we have initiated accurate numerical calculations of non-linear x-ray processes such as may be observed experimentally at new free-electron laser (FEL) facilities.

Early Career - Ultrafast Electron Diffraction from Aligned Molecules

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Students:	1 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$150,000

PROGRAM SCOPE

The goal of the project is to measure the three-dimensional structure and dynamics of isolated molecules in the gas phase. The project will provide a means to observe ultrafast dynamics in real space and time in previously inaccessible systems. A new method to capture the three-dimensional structure and dynamics of molecules with atomic resolution will be implemented. The method uses ultrafast electron diffraction and laser-induced alignment to target molecules and ultrafast reactions that cannot be imaged by other methods.

Electron diffraction from molecules in the gas phase has been a successful technique for determining the structure of isolated molecules. However, due to the random orientation of the molecules in the gas phase, only one-dimensional information (the interatomic distances) can be retrieved from the diffraction patterns. The resulting loss of information limits the size of molecular structures that can be investigated. The experimental method proposed here solves this problem by combining two existing techniques: ultrafast electron diffraction and non-adiabatic laser alignment of molecules. It is known that if the molecules are not randomly oriented but aligned along a given direction, the three-dimensional molecular structure becomes accessible. The idea consists of recording multiple diffraction patterns by rotating the alignment axis, each one corresponding to a different projection of the molecule. A three-dimensional image of the structure can be retrieved by merging the information from multiple diffraction patterns.

FY 2012 HIGHLIGHTS

We have recently demonstrated, for the first time, three-dimensional imaging of isolated molecules with atomic resolution. We successfully retrieved a three-dimensional image of a symmetric top molecule (CF3I) from multiple diffraction patterns. The molecules were impulsively aligned with a femtosecond laser pulse, and a femtosecond electron pulse was used to capture a diffraction pattern. Multiple diffraction patterns were captured corresponding to different orientations of the molecule. The structure of the molecule was reconstructed by combining the information from multiple diffraction patterns.

Laser-Produced Coherent X-Ray Sources

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Funding:	$150,000

PROGRAM SCOPE

In this project, we experimentally and theoretically explore the physics of novel x-ray sources, based on the interactions of ultra-high-intensity laser light with matter. X-rays in the energy range 10 keV – 1 MeV can be produced by Thomson (inverse Compton) scattering of intense laser light with laser-accelerated electrons. Because the x-rays produced from such a source have sub-angstrom wavelength, and femtosecond pulse duration, they can provide information on the structure of matter with atomic-scale resolution, simultaneously on both the spatial and temporal scale lengths. Moreover, because the electron beam is accelerated by the ultra-high gradient of a laser-driven wakefield, the combined length of both the accelerator and wiggler regions is only a few millimeters. Consequently, such a source can have a university-laboratory-scale footprint. Matter under extreme conditions can be studied with pump-probe experiments with any combination of these x-ray, electron, or laser beams.

This project involves the physics at the forefront of relativistic physics and nonlinear optics. Applications include the study of ultrafast chemical, biological, and physical processes, such as inner-shell atomic processes, phase transitions, and vacuum-assisted ionization.

FY 2012 HIGHLIGHTS

In this phase of the project, we succeeded in generating MeV energy x-rays by means of Compton-scattering. Our design employs two independently adjustable laser pulses from the same high-peak-power laser system—one to accelerate electrons by driving a high-gradient laser wakefield and one to scatter. This allowed for independent optimization of the electron bunch and scattering laser pulse, both of which were spatially overlapped (and temporally synchronized) with micron (femtosecond) accuracy. The drive laser system delivers a peak power of > 100 TW at a repetition rate of 10 Hz. The laser-driven electron accelerator delivers beams with energy up to 800 MeV and divergence of 2 mrad. The total photon number achieved with our source was measured to be 2×10^7; the source size was 5 µm; and the beam divergence angle was ~10 mrad. The peak brightness is four orders of magnitude higher than obtained by conventional Compton sources. The x-ray photon energy, peaked at 1 MeV and reaching up to 4 MeV, exceeds the thresholds for fundamental nuclear processes (e.g., pair production and photodisintegration). The x-ray wavelength will be tuned to the angstrom range (the inter-atomic spacing), and the x-ray pulse duration will be minimized (< 10 fs). This combination can simultaneously provide spatial and temporal information with atomic-scale resolution.

Further, we developed our own benchmarked numerical code to calculate the angle-resolved x-ray spectrum, which compared well with the experimental results.

Energetic Photon and Electron Interactions with Positive Ions

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Funding: $165,000

PROGRAM SCOPE/FY 2012 HIGHLIGHTS

This experimental program addresses fundamental interactions of ultraviolet light with atomic and molecular ions using a dedicated merged-beams endstation at the Advanced Light Source (ALS). Monochromatized synchrotron radiation is used to study photoionization of positive ions at the ALS undulator beamline 10.0.1.2, enabling the electronic structure and dynamics of atomic and molecular ions to be quantitatively probed by photoion-yield spectroscopy. Due to their large numbers of identical atoms, nanometer size, and empty quasi-spherical cage structures, fullerene molecular ions are of particular interest as structural intermediates between individual molecules and solids, and exhibit some of the properties of each. Among those under investigation are strong resonances associated with collective excitation of plasmon oscillation modes involving several hundred valence electrons. The most recent emphasis has been on photoionization of so-called endofullerene molecular ions, in which an atom is confined within the fullerene cage. Such synthesized molecules have promising practical applications in energy research, quantum computing, and medicine. Confinement resonances associated with the interaction of energetic photons with “caged atoms” are predicted by numerous theoretical studies. The phenomenon is attributed to interference between direct photoelectron waves from the caged atom and waves reflected by the cage. Considerable disagreement exists concerning their relative phase and amplitude, and even their existence. A noble gas atom such as xenon does not form ionic bonds and is centered within a fullerene molecular cage. Xenon also exhibits a giant resonance in 4d inner-shell photoionization by extreme ultraviolet light, making caged xenon an ideal candidate for an experiment to resolve these fundamental questions. Since noble gas endofullerenes are not commercially available, a simple apparatus was developed to synthesize them in the laboratory prior to the measurements. Initial results with caged xenon ions ($Xe@C_{60}^{+}$) were strongly suggestive of the predicted confinement resonances. The objective has been to refine these measurements and their statistical precision as higher-yield endofullerene materials become available. A somewhat surprising result is the significant degree of fragmentation of the fullerene molecular cage that results when such a caged atom is excited by extreme ultraviolet light. Systematic studies have been under way with both fullerene and endofullerene molecular ions to probe the underlying mechanisms in more detail.

Use of isotopically enriched ^{136}Xe in the endohedral synthesis increased the yield of $Xe@C_{60}$ in the prepared endofullerene samples from 1:100,000 to 1:4000. This resulted in an increase of the $Xe@C_{60}^{+}$ ion beam intensity by a factor of 40, yielding correspondingly higher photoion count rates. The statistical precision of the resulting data was dramatically improved, clearly defining the multi-path interference structure and permitting a systematic exploration of the product ion states: $Xe@C_{60}^{3+}$, $Xe@C_{58}^{3+}$, $Xe@C_{56}^{3+}$, $Xe@C_{54}^{3+}$, $Xe@C_{60}^{2+}$, and $Xe@C_{58}^{4+}$. The net Xe 4d photoionization contribution exhibited an identical interference pattern for all triply charged products. The Xe 4d feature was absent for doubly charged products and exhibited no interference structure for the quadruply ionized product. These findings are consistent with the multipath interference model and unambiguously establish the existence of confinement resonances. Theoretical calculations indicate that the interference pattern is strongly dependent on the C_{60} cage diameter and thickness.

Combining High Level Ab Initio Calculations With Laser Control of Molecular Dynamics

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Funding:	$120,000

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. We are applying the techniques and understanding we have developed to dissociative ionization pump-probe spectroscopy and pulse shape spectroscopy.

FY 2012 HIGHLIGHTS

(1) Local vs. Non-Local Dynamics: Our pump probe measurements, which follow ultrafast relaxation in DNA bases following excitation in the deep UV, have revealed non-local evolution of the wave function on the excited state surfaces for uracil, cytosine, and adenine. We performed quantum dynamics calculations on simple two-dimensional model potentials in order to understand the features of the excited state potentials which can lead to the kind of non-local relaxation that we observed in experiments.

(2) Dyson Orbitals in Strong Field Ionization: Our pump probe measurements described above rely on strong field ionization in order to probe the dynamics on the neutral excited state. The ionization of these excited state molecules is interesting both as a probe of the neutral excited state dynamics and as a fundamental issue in strong field ionization—in particular as a probe of correlations between initial and final states in strong field ionization. In collaboration with Michael Spanner and Sergeui Patchovskii at the National Research Council of Canada (who have carried out detailed calculations of strong field ionization for the molecules we are working on), we have studied the role of Dyson orbitals in strong field molecular ionization.

(3) Uracil Cation Fragmentation: A key ingredient in the analysis described above was an understanding of which molecular fragment ions originate from a given ionic state. We calculated the dissociation energies and transition state energies for several fragments from uracil and were able to associate several fragments with specific states of the molecular cation. *Ab initio* calculations on the ground ionic state of the uracil cation reveal that about 2 eV of energy is needed to produce m/z 69, while an energy of 4 eV will lead to smaller fragments with m/z 28, 41, 42.

(4) Two Dimensional Fourier Transform Spectroscopy: Our two dimensional Fourier transform spectroscopy measurements on adenine and uracil showed some differences in the evolution of the spectrum as a function of time delay for the two molecules, which we were able to interpret in terms of the gradient of the excited state surface near the Franck Condon region.

Toward Controlled Electronic Dynamics in Complex Systems

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Funding:	$110,000

PROGRAM SCOPE

Coherent molecular alignment by moderately intense laser pulses developed, during the past 15 years, from a theoretical dream into an active field of research with a rapidly growing range of applications in optics, physics, and spectroscopy. Our DOE-supported research during the past year can be broadly categorized into two conceptually and practically related topics: (1) extension of the concept of molecular alignment from the domain of isolated, rigid diatomic molecules to complex systems, including nonrigid molecules, large polyatomic molecules, solvated molecules, molecular assembly, and molecular junctions; and (2) development and application of theoretical and numerical tools to explore new opportunities in the area of high harmonic generation (HHG) from aligned molecules. The first topic was the thrust of our original DOE AMOS application. The second was motivated by the intense interest of the AMOS Program in attosecond science and rescattering electrons physics, and has been mostly carried out in collaboration with AMOS experimentalists colleagues.

FY 2012 HIGHLIGHTS

Within the first theme, we applied during the past funding period coherent alignment to chirality control, manipulation of nuclear spin isomers, control of electron transport via molecular junctions, a coherent approach to probe solute-solvent interactions, and a newly discovered field-induced molecular assembly phenomenon. Completion of this research, in the next funding period, will hopefully accomplish our ultimate goal of extending alignment from the domain of physics and optics to make a tool in material science, solution chemistry, and possibly engineering.

Within the second theme of our DOE-supported research during the past year, we collaborated with experimental AMOS colleagues at Stanford to address the problem of HHG from aligned asymmetric top molecules and with experimental AMOS colleagues at JILA to accomplish two projects in the field of HHG from aligned linear molecules: an approach to extract continuum electron dynamics from high harmonic emission, and an exploration of the origin of ultrafast dichroism, its surprising properties, and its application as a probe of molecular structure and electron dynamics. In addition, we continued our efforts to develop improved numerical methods to compute the electronic dynamics underlying HHG, and performed numerical work on the information content of the ellipticity of high-order harmonics.

This research has led to 12 publications during the past funding period, including 8 publications on the first topic and 4 on the second. These manuscripts were published in *Physical Review Letters*, *Physical Review A*, the *Journal of Chemical Physics*, and several invited article special issues.

Attosecond and Ultra-Fast X-Ray Science

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Funding:	$200,000

PROGRAM SCOPE

The goal of the program consists in generation, characterization, and application of short attosecond (1 attosecond = 10^{-18} sec) x-ray pulses for interrogating the fastest changes taking place in atoms and molecules. In the sports world, *controlling the clock* is an expression used to designate specific strategies teams use during the game in order to achieve favorable outcomes. Analogously, in the small world of atoms and molecules, controlling the clock in order to steer, for example, a chemical reaction on a desired path, requires a real-time intervention during the reaction. This can be accomplished by interacting a molecule with an attosecond x-ray pulse, whose duration is shorter than the reaction taking place. Developing the tools to view and ultimately control in real-time ultrafast phenomena to investigate fundamental aspects of light-matter interactions constitutes the scope of the program. Nonetheless, the attosecond x-rays, just as conventional, long-pulse or continuous sources, will also be beneficial for applied sciences, such as material processing, chemistry, or biology. Furthermore, the interdisciplinary nature of this research, coupled with state-of-the-art ultra-fast optical engineering, provide an excellent training ground for both undergraduate and graduate students. Former group members are contributing to various sectors of science and technology in academia, national laboratories, and the private sector.

FY 2012 HIGHLIGHTS

The team completed two data runs at Linac Coherent Light Source (LCLS) aimed at developing x-ray free electron laser metrology techniques. In particular, overlapping the LCLS x-ray pulses with weak infrared pulses, the team demonstrated shot-to-shot streaking of Auger electron emission. At OSU, in collaboration with Prof. David Reis from Stanford, the team completed a series of experiments exploring high harmonic generation in crystals. This new scheme opens the door for compact, table-top, all-solid-state XUV attosecond sources.

Spatial-Temporal Imaging During Chemical Reactions

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Miller, Terry, Ohio State University
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Funding: $222,000

PROGRAM SCOPE

Chemical reactions happen all the time and everywhere and have tremendous impact on our daily lives. They are closely involved in purifying the water we drink, in cooking the food we eat, in the air we breathe, in the development and production of medicines to help promote good health, in the microchips and batteries in computers and laptops, and in the steel, aluminum, rubber, glass, and plastic used in housing and automobiles. Controlling the chemical reactions while discovering new ways of material transformations to improve our daily lives is a direction mankind has been working toward for centuries. Therefore, studying and understanding chemical reactions continue to be important endeavors for the future, and it has been a dream of chemists and physicists to directly “watch” the movement of atoms and molecules inside the matter during its transformation.

Modern motion pictures are formed by viewing a sequence of still images in succession at a rate of 24 frames per second. Each frame provides part of the action; the time between frames is called the temporal resolution—in this case, 1/24 second. At the same time, we define the spatial resolution to be the smallest object one can discern. Atoms and molecules move and interact with each other on the femtosecond time scale; a time that is almost unfathomable to humans. We are developing a new fast “camera” using strong laser pulses that allow us to record the motion of atoms and molecules during chemical reactions with spatial resolution comparable to the size of the atom (10 billion atoms side by side cover 1 meter) and temporal resolution of 1 femtosecond (10^{15} femtosecond=1 second).

FY 2012 HIGHLIGHTS

We have developed a novel imaging technique called laser-induced electron diffraction using very short strong laser pulses. This electron-based “camera” has a shutter speed comparable to the atomic motion, and it helps us to take the first freeze-frame images of atoms vibrating in oxygen and nitrogen molecules. The oscillating electric field of the laser pulse couples energy into the molecule and rips off an electron. This electron will later be fired back into its mother molecule when the electric field changes its direction, serving as a “flash bulb” to illuminate the atomic motions within the molecule. This technique obtained an exquisite spatial (atomic-sized) and femtosecond (10^{-15} second) temporal resolution and offers a novel method for capturing the transformation of molecules through the manipulation of one of its own electrons. Now the next steps are to make it work for more complex molecules and control chemical reactions.

Control of Molecular Dynamics: Algorithms for Design and Implementation

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Funding:	$130,000

PROGRAM SCOPE

This research program is concerned with conceptual and algorithmic developments addressing control over quantum dynamics phenomena. Theoretical and computational studies are the focus, with the ultimate significance being their implications in associated laboratory experiments. The program aims at developing a deeper understanding of quantum control and providing new algorithms to enhance laboratory control capabilities.

FY 2012 HIGHLIGHTS

We have examined the topology of quantum control landscapes for taking an initial state to a final state, where the state either may be pure, an ensemble density matrix, or a unitary propagator. We have particularly formulated the quantum control landscape theory to assess the ease of finding optimal control fields in simulations and in the laboratory. The necessary and sufficient conditions were analyzed for encountering so called singular critical controls that might hinder a climb of the landscape. Simulations were performed showing that all of the numerically identified landscape critical controls are not traps, in support of empirical observations on the ease of finding high-quality optimal control fields. Finally, studies were initiated to understand how constraints upon the controls might influence the practical ability to reach high levels of control fidelity. Simulations and analysis indicate a good practical degree of robustness to resource limitations.

Recent work explored the possibility of directly manipulating laser-driven nuclear excitations from a quantum control perspective. The controllability of laser-driven electric dipole and magnetic dipole transitions among pure nuclear states was analyzed. Within a set of realistic and general conditions, atomic nuclei were demonstrated to possess full-state controllability. Additionally, an analysis of the nuclear state excitation probability as a function of the laser control field was conducted. We showed that the nuclear control landscape possesses a generic topology, which has important physical consequences for achieving optimal nuclear state excitation with intense laser fields. We also provided an assessment of the technological challenges that need to be considered when implementing direct nuclear control in the laboratory.

Antenna-Coupled Light-Matter Interactions

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Funding:	$135,000

PROGRAM SCOPE

We study light-matter interactions in nanoscale environments. More specifically, we are interested to further develop the 'optical antenna' concept to locally control the generation and absorption of light. Optical antennas are devices that convert free-propagating optical radiation to localized energy, and vice versa. They are being studied for enhancing the efficiency of photo detection, light emission, sensing, heat transfer, and spectroscopy. Similar to their radiowave and microwave analogues, optical antennas optimize the energy transfer between a localized source or receiver and the free radiation field.

A key goal of this project is the development of an understanding of how a quantum mechanical system interacts with a mesoscopic structure (antenna) at very close separations. To optimize the coupling between a quantum emitter (atom, molecule, ion, defect center, etc.) and an optical antenna, we will explore concepts of impedance matching developed in classical antenna theory. Optimized antenna-emitter coupling will lead to ultrabright and directional photon sources, which are of interest to various fields of research.

Most of the optical antenna structures studied to date operate on a 'light-in / light-out' basis. However, in the traditional radiofrequency and microwave regime, antennas are usually employed to convert electromagnetic radiation to electric currents, and vice versa. We are therefore interested to explore the possibility of antenna-coupled electro-optical transduction, i.e., processes in which electrons are locally converted into photons, and vice versa. We will explore optical rectification at metal-metal tunneling junctions to directly convert incident photons to electrons (optical rectennas) and study electron-plasmon coupling to convert tunneling electrons to photons.

Our work is firmly rooted on our previous experiments that have demonstrated controlled fluorescence enhancement and quenching of a single, optically excited, quantum emitter. The objective is to take this research to the next level and study antenna-coupled electro-optical transduction. The knowledge attained through this project will be important for the development of high-efficiency optoelectronic devices, ranging from photovoltaics to light-emitting devices.

Atomic and Molecular Correlation in Strong Fields

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Funding:	$100,000

PROGRAM SCOPE

We are interested in understanding how very intense laser light couples to atoms and molecules. Theoretical study faces substantial challenges in this domain. These arise from the combination of the high intensity, fully phase-coherent character and short-time nature of the laser pulses in current use, where the laser's electric-field force roughly matches the Coulomb forces among electrons and the nucleus. An important additional challenge arises when there is a need to account for more than one dynamically active electron.

FY 2012 HIGHLIGHTS

Our work in 2012 built on earlier results obtained from numerical experiments we carried out. These were studies of two, three, and four active atomic electrons in strong time-dependent and phase-coherent laser fields. Continuing this work in 2012, we used very large ensembles (1-10 million members) of classical multi-electron trajectories. Although classical, the technique is completely *ab initio* in the sense that it proceeds from a specific Hamiltonian description of a multi-electron model atom with empirically accurate ionization potentials matching those of familiar experimental target atoms (helium, neon, argon, xenon, magnesium) without simplifying dynamical approximations. The technique is capable of unique theoretical exploration. For example, in the domain of common high laser intensities, it has allowed comprehensive theoretical study of effects arising under elliptical polarization, and has provided new evidence relevant to questions of electron independence and correlation. We are currently attacking the possibility of breakdown of the single-active electron approximation. Our calculations are matching new results showing momentum distribution ``tilts" as recorded in experiments at ETH-Zurich.

Combining High Level Ab Initio Calculations With Laser Control of Molecular Dynamics

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Students:	0 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding:	$100,000

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. We are applying the techniques and understanding we have developed to dissociative ionization pump-probe spectroscopy and pulse shape spectroscopy.

FY 2012 HIGHLIGHTS

(1) Local vs. Non-Local Dynamics: Our pump probe measurements, which follow ultrafast relaxation in DNA bases following excitation in the deep UV, have revealed non-local evolution of the wave function on the excited state surfaces for uracil, cytosine, and adenine. We performed quantum dynamics calculations on simple two-dimensional model potentials in order to understand the features of the excited state potentials which can lead to the kind of non-local relaxation that we observed in experiments.

(2) Dyson Orbitals in Strong Field Ionization: Our pump probe measurements described above rely on strong field ionization in order to probe the dynamics on the neutral excited state. The ionization of these excited state molecules is interesting both as a probe of the neutral excited state dynamics and as a fundamental issue in strong field ionization—in particular as a probe of correlations between initial and final states in strong field ionization. In collaboration with Michael Spanner and Sergeui Patchovskii at the National Research Council of Canada (who have carried out detailed calculations of strong field ionization for the molecules we are working on), we have studied the role of Dyson orbitals in strong field molecular ionization.

(3) Uracil Cation Fragmentation: A key ingredient in the analysis described above was an understanding of which molecular fragment ions originate from a given ionic state. We calculated the dissociation energies and transition state energies for several fragments from uracil and were able to associate several fragments with specific states of the molecular cation. *Ab initio* calculations on the ground ionic state of the uracil cation reveal that about 2 eV of energy is needed to produce m/z 69, while an energy of 4 eV will lead to smaller fragments with m/z 28, 41, 42.

(4) Two Dimensional Fourier Transform Spectroscopy: Our two dimensional Fourier transform spectroscopy measurements on adenine and uracil showed some differences in the evolution of the spectrum as a function of time delay for the two molecules, which we were able to interpret in terms of the gradient of the excited state surface near the Franck Condon region.

Theory of Atomic Collisions and Dynamics

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Funding:	$125,000

PROGRAM SCOPE

Our program identifies new aspects of atomic dynamics related to the transfer of angular momentum. To that end methods are developed that simulate collisions of ions with one-electron atoms. Methods are also developed to compute angular momentum transfer between incident electrons and atomic or molecular targets.

FY 2012 HIGHLIGHTS

Our projects show how one can use the momentum distributions of atomic fragments measured using coincidence and reaction microscope experiments to image magnitudes of Schrodinger wave functions that encode the information about atomic collisions. This theory is called the *imaging theorem*, and our projects are directed towards showing how the theorem is used theoretically. Its use involves integrating the time-dependent Schrodinger equation to infinite times. We have developed programs to perform such integrations efficiently.

Our calculations show that the velocity field associated with Schrodinger wave functions may have singular points that are vortices. These vortices show up experimentally as isolated zeros of measured electron distributions. We further show that such vortices reflect angular momentum transfer in atomic dynamics. One notable example is provided by our proof that collisions with charged particles involve the transfer of effectively elliptically polarized photons. In some instances, this effective elliptical polarization is as high as 30%. This insight is used to interpret distributions of electrons ejected from inner shells by fast electrons.

High Intensity Femtosecond XUV Pulse Interactions with Atomic Clusters

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Funding:	$150,000

PROGRAM SCOPE

The goal of our experimental program is 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 of interaction is very different from interactions of intense IR pulses with clusters where the laser ponderomotive potential is significantly greater than the binding potential of electrons in the cluster. We perform these studies with an XUV source created by converting a high-energy (1.5 J) femtosecond laser to the short wavelength region through 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 2012 HIGHLIGHTS

We completed a long focal length HHG beamline on a 1.5 J. 35 fs, 10 Hz TI:sapphire laser. This new beam line has a long, 5 m focal length optic and vacuum transport to a solid cluster chamber. We have begun characterization of HHG yields and intend to begin studies of ion production from XUV pulses in oxide clusters (like SnO). We have also constructed the laser ablation module which is used to produce clusters from solids like the tin oxide.

Studies of Autoionizing States Relevant to Dielectronic Recombination

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Funding:	$148,000

PROGRAM SCOPE

In this research program, we are studying doubly excited autoionizing atomic states and the effects of intense low frequency radiation on atomic photoionization. A systematic study of autoionization allows us to understand the reverse process, dielectronic recombination (DR). DR provides an efficient recombination mechanism for ions and electrons in astrophysical and laboratory plasmas. The most important pathway for DR is through the autoionizing Rydberg states. Because Rydberg states are involved, DR rates are profoundly influenced by other charged particle collision processes and by any small electric and magnetic fields in the plasma. Consequently, a major thrust of this program has been understanding how autoionization rates and, thus, DR are affected by external fields. The use of a microwave field to mimic the rapidly varying fields which occur in electron collisions has led to the study of laser photoionization of atoms in strong microwave fields. We are exploring this problem since it is very similar to an atom in an intense infrared field exposed to a train of attosecond xuv pulses, a problem currently under investigation by many research groups.

FY 2012 HIGHLIGHTS

We have conducted the first measurements on autoionization in very weak electric fields. Specifically, we have examined the transitions from the bound Ba 6s17k states to the autoionizing $6p_{1/2}17k$ states in electric fields of less than 20 V/cm, in which only the $\ell>4$ states need be considered. In these low electric fields, the bound 6s17k states are composed of all the $6sn\ell$ states of $\ell>4$. In contrast, the autoionizing $6p_{1/2}17k$ states appear to be a set of discrete Stark states composed of $6p_{1/2}17\ell$ states of $\ell>5$ and a broad quasi continuum, the $6p_{1/2}17h$ state. Since the initial 6s17k state includes the 6s17h state, the excitation has an amplitude to the $6p_{1/2}17h$ continuum as well as to the discrete $6p_{1/2}17k$ Stark states; and we have treated the excitation using Fano's configuration interaction theory. A most interesting result of the measurements is that the 6s17k- $6p_{1/2}17k$ excitation spectrum appears to be entirely to the discrete states as k approaches 17, but almost entirely to the quasicontinuum as k approaches 5, an observation reproduced by the theory.

Earlier we showed that a wavepacket excited by a ps laser tuned above the ionization limit in the presence of a microwave field resulted in a bound atom if the ps laser excitation occurred at the correct phase of the microwave field. According to our simple classical model, just as excitation at the correct phase of the microwave field leads to removal energy from the photoelectron, at the opposite phase energy is given to the photoelectron. We have excited bound wavepackets in the presence of a microwave field, and we have observed the phase dependent population transfer to both higher and lower energy, as predicted by our classical model.

Using Strong Optical Fields to Manipulate and Probe Coherent Molecular Dynamics

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Funding:	$145,000

PROGRAM SCOPE

This project focuses on the exploration and control of non-perturbative dynamics in 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 molecules. Through the application of these methods, we are working to obtain a more complete picture of the non-perturbative response of molecules to strong fields.

FY 2012 HIGHLIGHTS

We (1) upgraded our laser system with the addition of a hollow-core fiber (HCF) compressor to enable the generation of <10fs pulses for use in our continuing multi-electron dissociative ionization experiments and for future attosecond pulse generation; (2) upgraded our supersonic molecular beam apparatus, including the installation of an Even-Lavie pulsed valve, to obtain substantially lower rotational temperatures (~1K) for our continuing molecular orientation experiments; (3) characterized a source of intense, single-cycle THz pulses based on optical rectification of high-energy, 100 fs, 800nm laser pulses in MgO-doped LiNbO3 for use in experiments seeking to produce samples of well-oriented gas-phase molecules and for time-resolved manipulation of continuum electron wavepackets; (4) began an exploration of intense ionization of atoms in the extreme low frequency regime using intense single-cycle THz pulses; and (5) began experiments exploring the use of combined optical and THz fields to induce high-contrast field-free molecular orientation.

New Scientific Opportunities Through Inelastic X-Ray Scattering at 3rd-and 4th-Generation Light Sources

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Funding: $75,000

PROGRAM SCOPE

This research program encompasses two technically-related thrusts, each involving the further development and implementation of high-throughput inelastic x-ray scattering (IXS) methods towards specific scientific goals. First, we are performing a combination of experimental and theoretical work on the nonresonant IXS from valence excitations (i.e., *Compton scattering* in CM physics and *x-ray Thomson scattering* in plasma physics). This research will provide a new first principles method to calculate the Compton profile line-shape in molecular and condensed phase studies while also critically testing the accuracy of existing methods to determine the state variables of warm dense matter, such as in XFEL and large-scale laser facility experiments. Second, we are continuing work aimed at expanding the scope and range of applications of x-ray emission spectroscopy, especially under time-resolved and other extreme conditions. To this end, using instrumentation developed under this award, we are pursuing time-resolved XANES studies of the 4f electronic state of lanthanide-doped phosphors; time-resolved XANES studies of the metal-insulator transition in single-crystal VO_2 nanobeams; time-resolved XANES studies of the largely unexplored S4 intermediate state of photosystem II; and high-pressure studies of 4f delocalization at the volume collapse transition of lanthanide elements. Further enhancement of these technologies are important proposed components of the Advanced Photon Source upgrade plan (APS-U), are relevant for several beamlines at NSLS-II, and may be useful at the LCLS.

FY 2012 HIGHLIGHTS

We have demonstrated that miniature x-ray spectrometers (miniXES) can be advantageously used in high-pressure experiments, such as in the study of the volume collapse in lanthanide materials, where they provide more than a factor of ten improvement in count rates over traditional x-ray emission spectrometers.

We have completed the development of a real-space Green’s function approach to the calculation of the Compton profile for inelastic x-ray scattering. This complements existing band-structure based methods by allowing easy calculation of both ordered and disordered systems, and furthermore allows straightforward extensions to self-consistent finite-temperature calculations, such as are needed for x-ray Thomson scattering studies of warm dense matter and other dense correlated plasmas.

Probing Complexity using the ALS and the LCLS

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Students:	2 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$200,000

PROGRAM SCOPE

The research program objective is to investigate fundamental interactions between photons and gas-phase systems to advance our understanding of correlated and many body phenomena. Our research investigations focus on probing multi-electron interactions in order to understand and ultimately control energy transfer processes from electromagnetic radiation. Most of our work is carried out in a strong partnership with theorists.

Our current interests include two studies. The first is the study of non-linear and strong field phenomena in the x-ray regime using the linac coherent light source (LCLS), the most powerful ultra-fast x-ray free electron laser (FEL) facility in the world located at the SLAC National Laboratory. Our investigations focus on probing physical and chemical processes that happen on ultrafast time scales. This is achieved by examining both electronic and nuclear dynamics subsequent to the interaction of molecules and clusters with LCLS pulses of various intensity and pulse duration. The second is the study of correlated processes in select molecules and anions with vuv-soft x-rays from the Advanced Light Source (ALS) at Lawrence Berkeley Laboratory.

FY 2012 HIGHLIGHTS

Theory predicted twenty-five years ago that double-core hole (DCH) spectroscopy can provide a new powerful means of differentiating between similar chemical systems with sensitivity not hitherto possible. We were able to demonstrate the feasibility of this methodology by measuring, for the first time, two-site DCH in molecules (CO, CO_2, N_2O), produced via sequential two-photon absorption, using short, intense x-ray pulses from the LCLS. We have also carried out experiments in larger systems such as pyrimidine and formamide. This data is presently being analyzed. The DCH work represents a rebirth of electron spectroscopy for chemical analysis (ESCA). It impacts chemical analysis since it introduces a powerful method to measure the structure and dynamics of similar systems unambiguously.

We also carried out in May an experiment at LCLS that consists of forming a nanoplasma and probing its evolution when C_{60} molecules are ionized with intense, short pulse duration that varied between 5-180 fs. The impact of this work is to provide an atomic & molecular view of matter under extreme condition. The latter is present in cores of large planets, systems that start solid and end as a plasma, x-ray driven inertial fusion experiments, supernovae and stellar interiors.

Structure from Fleeting Illumination of Objects in Flight

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Students:	1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$75,000

PROGRAM SCOPE

It is now possible to intersect molecules, viruses, and cells “in flight” with intense short pulses of radiation from x-ray free electron lasers (XFELs), and record “snapshots” before the object is destroyed. We are developing a new generation of powerful algorithms to recover structure and dynamics from such ultra-low-signal random sightings. These techniques, based on concepts from differential geometry, general relativity, graph theory, and diffraction physics, promise to revolutionize our understanding of structure and function in biological and energy-synthesis processes.

FY 2012 HIGHLIGHTS

X-ray free electron lasers provide exquisitely short (~ 1fs), intense pulses of radiation ideal for studying ultrafast processes in physics, chemistry, and biochemistry. Time-resolved experiments, however, rely on placing the system under investigation in a precisely controlled state by means of a “pump” pulse and probing the system after a suitable delay. The ultimate time resolution is thus determined by the capability to control the delay between the pump and probe pulses. Due to the stochastic nature of processes underlying the generation of ultrashort x-ray pulses, however, the pump-probe timing inaccuracy exceeds the length of the x-ray pulse by up to two orders of magnitude. This substantially degrades the capability of most pump-probe techniques using x-ray laser probes. In collaboration with Bucksbaum et al., we are developing sophisticated mathematical techniques to extract dynamical information on time scales beyond current techniques.

Interactions of Ultracold Molecules: Collisions, Reactions, and Dipolar Effects

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Students:	0 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding:	$135,000

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 2012 HIGHLIGHTS

We recently discovered a simple method to produce ultracold RbCs in its absolute ground state, and in Fiscal Year 2012, we have focused on the study of this method as a means to produce large trapped samples of RbCs. In this method, we drive photoassociation (PA) transitions into tightly-bound states that decay with high probability to the absolute ground state. PA to such states was previously considered impractical due to the negligible probability for two colliding atoms to be sufficiently close. However, the usual assumptions used to calculate PA rates (WKB approximation for the scattering wavefunction) prove to be invalid at short range, and in fact, the process can be quite efficient. We observe high rates of formation of RbCs into low-lying vibrational levels, including the absolute ground state, through intermediate PA resonances that are well-characterized from previous spectroscopy. We have developed a detailed model that successfully describes both the PA rate and the subsequent population of the absolute ground state.

This method should make it possible to produce and accumulate absolute ground-state RbCs molecules into an optical trap, using the dissipation associated with decay of the PA resonance. Key to this approach is that RbCs is immune to inelastic collisions with itself and with Cs atoms. Hence, molecule production in the presence of dense Cs vapor can allow the accumulation of large molecular samples. In addition, the Cs atoms can act as a “scrubber” to remove residual rovibrationally-excited RbCs molecules that otherwise accumulate in the trap, via inelastic collisions. We plan to explore the dynamics of the accumulation and scrubbing processes in an optical trap next.

DOE National Laboratories

Atomic, Molecular and Optical Physics	
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Students:	2 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$1,825,000

PROGRAM SCOPE

The AMO physics program aims for quantitative understanding of x-ray interactions with isolated atoms and molecules from the weak-field limit explored at the APS to the high-intensity regime newly accessible at the Linac Coherent Light Source (LCLS), the world's first hard x-ray free electron laser.

During the past funding period, the AMO program has been instrumental in early experiments at the LCLS in establishing mechanisms of high-intensity, non-linear x-ray interactions with matter. In the coming funding period, the AMO physics program plans experiments at LCLS investigating the nature of the electronic response in atoms using seeded vs SASE pulses at intensities approaching 10^20 W/cm^2. The seeded pulses currently operate in the energy range 7-9 keV, are temporally coherent, and have a bandwidth approximately 40 times smaller than the SASE pulses. These differences are expected to alter the atomic response to ultraintense x-rays in ionization pathways and to lead to a clear manifestation of Rabi flopping. The AMO physics program also plans time-domain measurements of femtosecond inner-shell decay processes at LCLS and the understanding of inner-shell vacancy cascades in isolated molecular systems where interatomic Coulombic decay may play a critical role in exacerbating x-ray damage.

Ultrafast X-Ray Imaging of Laser-Controlled Molecular Motions

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Students:	4 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$847,000

PROGRAM SCOPE

The program Ultrafast X-ray Imaging of Laser Controlled Molecular Motions aims to develop novel techniques to use the full flux of the Advanced Photon Source (APS) for time-resolved x-ray measurements, using x-ray probes operating in the linear regime. By combining high-repetition-rate optical lasers with the MHz repetition rate of the x-ray pulses from the APS, the statistics available for studying laser-induced dynamics is equivalent to that used to study static structures. One current focus is on the study of the solvation dynamics, spin crossover, and photoinduced ligand exhange in molecules in solution. Simultaneously this task is developing methods to hold nanoobjects in solution phase, as a prelude to x-ray scattering studies from single nanoobjects to investigate dynamics with atomic-scale resolution. These dynamical processes are well suited to the Short Pulse X-ray Facility, an integral component of the APS Upgrade that will produce tunable, polarized, few picosecond pulses from the soft to the hard x-ray range.

Atomic, Molecular and Optical Sciences at LBNL

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Weber, Thorsten, Lawrence Berkeley National Laboratory
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Funding: $1,485,000

PROGRAM SCOPE

The goal of the program is to understand the structure and dynamics of atoms and molecules using photons and electrons as probes. The current projects are focused on (1) studying inner-shell photo-ionization of atoms and molecules, (2) providing a modern theoretical approach on a broad range of collision processes that are important in electron-driven chemistry, and (3) the probe fundamental atomic and molecular process involving low energy electrons interacting with molecules. The experimental and theoretical efforts are designed to break new ground and to provide basic knowledge that is central to the programmatic goals of BES/DOE. Unique LBNL facilities such as the ALS and NERSC are used to perform experimental and computational work. We seek to obtain new insight into atomic and molecular processes and to test advanced theoretical treatments by achieving new levels of completeness in the description of the distribution of momenta and/or internal states of the products and their correlations. The experimental studies are carried out with a powerful Cold Target Recoil Ion Momentum Spectroscopy (COLTRIMS) technique. We also seek to develop the theoretical and computational tools for treating electron and photon interactions with targets that are presently beyond the grasp of *ab initio* methods and develop new methods for studying electron interactions with polyatomic molecules, complex molecular clusters, and ultimately, molecules bound to surfaces.

FY 2012 HIGHLIGHTS

- Photoionization and Dissociative Electron Attachment to Small Molecules: Experimental Program
- Electron– and Photon–Driven Processes in Physics and Chemistry

Early Career-Ultrafast X-Ray Studies of Intramolecular and Interfacial Charge Migration

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

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 will be combined with studies at 4th generation light sources, such as the Linac Coherent Light Source, and complementary measurements at 3rd generation synchrotrons, such as the Advanced Light Source.

Ultrafast X-Ray Science Laboratory (UXSL)

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Students:	8 Postdoctoral Fellow(s), 6 Graduate(s), 0 Undergraduate(s)
Funding:	$2,120,000

PROGRAM SCOPE

The Ultrafast X-ray Science Laboratory (UXSL) applies new ultrafast x-ray sources to problems of central interest to chemistry and atomic and molecular physics with the goal of understanding electron dynamics and chemical transformations on their intrinsic time scales in the gas and condensed phases. Current projects focus on (1) soft x-ray femtosecond HHG sources, including a new high repetition rate high harmonic source and its use in time-resolved photoelectron spectroscopy of molecules and clusters; (2) applications of a new ultra-fast x-ray science facility at the Advanced Light Source at LBNL, primarily to experiments using novel time-resolved x-ray spectroscopic techniques to understand solution-phase molecular dynamics; (3) applications of high-intensity HHG sources as well as femtosecond x-rays at the Advanced Light Source to problems in atomic and molecular physics that include nonadiabatic dynamics in photoexcited polyatomic molecules and time-resolved spectroscopy detecting both electrons and ions; **(**4) theory and computation in which the dynamics of electrons and atoms in intense short pulses together with extensions of electronic structure methods and their combination with nonadiabatic direct dynamics both support and guide new experiments in the UXSL; and (5) attosecond atomic and molecular science in which the timescale of electronic transitions and correlation will be addressed directly using HHG sources and streak field methods. The set of experimental and theoretical projects that constitute the UXSL 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 2012 HIGHLIGHTS

- Ultrafast Soft X-Ray Chemical Dynamics
- Atomic, Molecular and Optical Sciences
- Ultrafast X-Ray Studies of Condensed Phase Molecular Dynamics
- Theory of Short Pulse Interactions, and the Determination of Electronic Excited States
- Attosecond Atomic and Molecular Science

Engineered Electronic and Magnetic Interactions in Nanocrystal Quantum Dots

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Funding:	$800,000

PROGRAM SCOPE

Using nanocrystal quantum dots, one can produce extremely strong spatial confinement of electronic excitations, a regime not accessible with other types of nanostructures. Because of this confinement, electronic energies in nanocrystals are directly dependent upon their dimensions, which is known as the quantum-size effect. This effect has been a powerful tool for controlling spectral responses of nanocrystals, enabling potential applications such as multicolor labeling, optical amplification, and low-cost lighting. Additionally, strong spatial confinement results in a significant enhancement of carrier-carrier interactions that lead to a number of novel physical phenomena, including large splitting of electronic states due to electron-hole exchange, ultrafast mutiexciton decay via Auger recombination, and “giant” exciton-exciton repulsion. Confinement-induced mixing between the conduction and the valence band can also result in interesting peculiarities in magnetic interactions, such as “giant” sign-switchable *g*-factors in magnetically doped NCs. Understanding the physics of electronic and magnetic interactions under conditions of extreme quantum confinement and the development of methods for controlling these interactions represent the major thrusts of this project. Research topics explored here include control of Auger recombination via engineered exciton-exciton interactions in heterostructured and alloyed nanocrystals with a goal of realizing continuous-wave lasing, new functional behaviors via nanocrystal doping with optically and electronically active ions, control of single-exciton dynamics via tunable fine-structure excitonic splitting, and controlled exchange interactions in magnetically doped NCs probed by steady-state and time-resolved magneto-optical spectroscopies.

FY 2012 HIGHLIGHTS

Research activities in this project have involved spectroscopic and magneto-optical studies of semiconductor NCs doped with transition-metal impurities. By incorporating small amounts of manganese or copper ions into the NCs, we have been able to achieve a high level of control over their optical and magnetic properties, and to realize novel regimes of magneto-optical interactions. One exciting piece of work relates to our recent research into the chemistry and spectroscopy of Cu-doped core/shell ZnSe/CdSe nanostructures. Specifically, via comprehensive steady-state and ultrafast optical characterization complemented by spectro-electrochemical measurements [Nano Lett. 11, 4753–4758 (2011); Nano Lett. 12, 4372–4379 (2012)], we have demonstrated that copper impurities are incorporated into the NCs as Cu^{2+} ions and represent a source of electronic charges (holes) that can interact with intrinsic conduction and valence-band states. These interactions lead to new functionalities (e.g., dual-color emission and a “giant” apparent Stokes shift) that can allow for the realization of interesting regimes of zero-threshold optical gain and “electron-only” light-emitting diodes.

Further, we used magnetic circular dichroism to show, for the first time, that Cu-doped NCs represent a new class *of diluted magnetic semiconductors.* Our recently published results [Nature Nano. doi:10.1038/nnano.2012.210 (2012)] demonstrate that in addition to strong magnetic exchange coupling between electrons/holes and embedded copper, these NCs exhibit a pronounced and persistent photo-induced magnetization. That is, *light* can control and increase (by over 100%) the NCs’ magnetization, suggesting the feasibility of new approaches to magnetic storage in which magnetically encoded information is manipulated not by magnetic fields but rather using much more flexible optical illumination.

Understanding and Controlling Atomic Scale Matter

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Vane, C. Randy, Oak Ridge National Laboratory
Students: 0 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding: $600,000

PROGRAM SCOPE

The overarching theme is development of fundamental understanding of the interactions of atomic scale systems, such as photon-atom, ion-atom, ion-ion, or ion-solid collisions, and use of this knowledge to develop systematic control of these systems. Specific focuses involve particle-solid/surface interactions, atomic processes in plasmas, and manipulation and control of atoms, molecules and clusters. Experiments are centered at the ORNL Multicharged Ion Research Facility (MIRF), with research augmented at off-site facilities offering ions and conditions suited to extensions of MIRF-based studies. Dissociation interactions of molecular ions at very low energies are studied using merged-beams capabilities at the MIRF and at international ion storage rings. Higher energy electron-molecular ion interactions are also studied at MIRF employing crossed-beams capabilities. MIRF ion-atom merged beams measurements spanning 0.1 to 1000 eV/u provide benchmarks for energy relevant sciences and tests of theory; ion-surface collisions are studied to understand surface scattering and modification; and theory is pursued to explore dynamics of strongly perturbed systems requiring new insights and mathematical and computational techniques. Recent progress includes upgrading the MIRF providing higher ion energies, expanding the number of experimental endstations, and developing new capabilities for preparing intitial states of atomic and molecular ions through new ion and neutral beam sources, as well as new methods for storing and cooling internal states of molecular ions. Overall, this project aims to expand the scientific knowledge base for new and improved energy technologies and their impact on the environment.

FY 2012 Highlights

We have collaborated with the Max-Planck-Institute for Nuclear Physics (MPIK) in Heidelberg, Germany, to design the first neutral injection beam line for a cryogenic storage ring. This will permit state-resolved collision experiments for fundamental molecular ions with neutral beams of, e.g., H and C at meV/u collision energies.

Ultrafast Chemical Science

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Students:	10 Postdoctoral Fellow(s), 8 Graduate(s), 0 Undergraduate(s)
Funding:	$3,152,000

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 2012 HIGHLIGHTS

The Ultrafast Chemical Science Program made significant progress, with highlights in each of its six subtasks during FY 2012. In ultrafast chemical theory, we have extended the capabilities of the AIMS method to describe time-resolved photoelectron spectroscopy type experiments with an emphasis on those involving high energy probe pulses. In attosecond science, we showed that the high harmonics of water can be used to track sub-femtosecond nuclear motion launched via ionization of the inner valence orbital. In solution phase chemistry, we investigated the dynamics of electron localization in time-resolved UV pump mid-IR probe spectroscopy for excited state ligand-to-metal charge transfer. We had 5 additional LCLS beam times devoted to our nonperiodic imaging activity, which now has more than 12 publications in print on imaging nanoscale structure at LCLS. In our nonlinear x-ray optics activity, we reported observations of nonlinear x-ray-optical sum frequency generation and also collected data at LCLS which clearly showed nonlinear Compton scattering for the first time as well as the first x-ray frequency doubling at the SACLA FEL in Japan. And in strong field amo physics, we completed LCLS studies which demonstrate for the first time the production of coherent states during x-ray absorption and Auger emission in molecules.

Catalysis Science

Institutions Receiving Grants

High Temperature Chemistry of Aromatic Hydrocarbons

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Sr. Investigator(s):	
Students:	2 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding:	$165,000

PROGRAM SCOPE

The long-range objectives of this research are 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. Some of the studies make use of readily available compounds; however, most require multi-step organic syntheses of key materials. 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. 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. Much is already known about the normal chemistry of hydrocarbons under ambient conditions, but much 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 or the minimization of an undesirable one, requires a clear knowledge of the basic chemistry that governs the fate of the species involved.

FY 2012 HIGHLIGHTS

We used high temperature gas phase chemistry to synthesize the first short, rigid, isomerically pure carbon nanotube by rational design. We also discovered reaction conditions that promote the reversibility of the Ir-catalyzed borylation of PAHs by C–H activation, and we showed how this new reaction protocol can be used to polyborylate PAHs to their maximum capacity. Finally, we also found that the Pd-catalyzed arylation of corannulene by C–H activation can be pushed to 100% replacement of all hydrogen atoms by aryl groups. An x-ray crystal structure of decakis (4-chlorophenyl) corannulene reveals that the extreme crowding of the ten aryl groups around the perimeter of the molecule flatten the normally bowl-shaped corannulene nucleus to an almost planar geometry. The ability of such direct Pd-catalyzed arylations to introduce so much strain into molecules was not previously recognized.

Catalysis, Dynamics, and Stability of Enzymes Under Extreme Conditions

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Funding:	$170,000

PROGRAM SCOPE

Conformational transitions in enzymes are key to function. The long-term goal is to achieve a more general understanding of the physical basis underlying the energy landscape of enzymes. We will characterize the influence of external physical parameters such as temperature, pressure, and solvent on protein dynamics, stability, and the linkage to catalysis, as well as learn lessons from nature on how proteins have adapted to extreme conditions. We anticipate that a deeper understanding of energy landscapes of the studied model enzymes will have direct impact in the rational design of biocatalysts and chemical catalysts, particularly with desired properties such as increased heat stability or pressure resistance.

Specific objectives for the previous years were to (1) apply the string method to the conformational transition of the kinase NtrC and adenylate kinase and calculate free energy landscapes, (2) complete the analysis of the transition state ensemble from high pressure NMR experiments and MD simulations, (3) investigate the role of water in the active site of adenylate kinase, (4) investigate the energetic contribution of Mg2+ and other metals to the phosphoryl transfer and lid-opening, and (5) analyze single molecule FRET experiments during turnover.

FY 2012 HIGHLIGHTS

We developed all methods that allow us to quantitatively measure the free energy landscape of an enzyme during catalysis using adenylate kinase as our model system. First, the combination of single turnover pre-steady state kinetics using a quenched flow machine, NMR dynamics during catalysis, and x-ray crystallography enables the detection of all individual steps in the enzymatic cycle (manuscript under review). Second, through a combination of quantum mechanical calculations and designed new experiments based on the computational results, we are getting a good understanding of the energy landscape of catalysis of the phosphoryl transfer in the active site. Of particular interest are our findings about the role of the nature of the divalent cation for catalysis. Third, we are in the process of learning the role of second shell residues on the catalysis of the chemical step.

In an effort to apply these catalytic strategies we have learned to rational enzyme design, we have started two new directions. The first is the reconstruction of how adenylate kinases have evolved on nature by developing a tree for the evolution of hyperthermophilic, mesophilic, and psychrophilic Adk. Preminary data are encouraging for unraveling the mechanisms adaptation to different temperatures.

For the second, in collaboration with D. Hilvert, we are studying the catalysis of a designer enzyme for the Kemp elimination and a consequently evolved one via selected evolution. The goals are to understand how to further improve this designer enzyme and then how to incorporate these new principles in the design protocol.

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

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Sr. Investigator(s):	
Students:	1 Postdoctoral Fellow(s), 1 Graduate(s), 2 Undergraduate(s)
Funding:	$150,000

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 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 2012 HIGHLIGHTS

We explored a variety of research areas as part of the overall program goal. We have investigated sigma-bond activation processes with our Zr/Co complexes, particularly the activation of the element-hydrogen bonds in alcohols, hydrazines, and thiols. We have also investigated our Zr/Co complexes as catalysts for the hydrosilylation of ketones and aldehydes. These complexes are not only competent catalysts, they have been shown to operate through a unique one-electron radical mechanism which, to our knowledge, is undocumented in the literature.

We have also continued to investigate some of the fundamental reaction steps associated with a hypothetical catalytic cycle for carbon dioxide reduction. Most importantly, we learned that while the oxophilicity of the early transition metal in our early/late heterobimetallic complexes is important for the initial CO_2 activation step, this same property hinders further functionalization or catalytic turnover. Thus, we began targeting different metal-metal combinations and have now extended our Zr/Co chemistry to V/Fe and Cr/Fe combinations. These complexes have unusually strong multiple bonding between the disparate metal atoms and have shown multielectron redox chemistry which is promising for small molecule activation studies. Along these lines, we have also begun to investigate whether two identical metal ions in different coordination environments (amide vs. phosphine) can facilitate some of the same cooperative reactivity achieved with early/late heterobimetallic complexes.

Synthetic and Mechanistic Investigations of Olefin Polymerization Catalyzed by Early Transition Metal Compounds

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Funding:	$185,000

PROGRAM SCOPE

The goal of this project is to develop new catalysts and provide understanding of ligand effects on catalyst composition in order to guide development of superior catalyst systems for polymerization of olefins. Our group is designing and synthesizing new "LX_2","pincer" type ligands and complexing early transition metals to afford precatalysts. In a collaboration with Hans Brintzinger from the University of Konstanz, we are also examining the structures of the components of catalyst systems obtained from reaction of zirconocene dichlorides with aluminum alkyls and aluminum hydrides. Such systems are currently used commercially to produce polyolefins, but the nature of the active and dormant species as well as the mechanisms of their interconversions are not understood. New information on catalyst design and performance may lead to new types of polymers and/or new chemical transformations between hydrocarbons and transition metal centers, ultimately contributing to the development of catalytic reactions for the production of fuels, commodity, and polymeric materials.

FY 2012 HIGHLIGHTS

We are currently making good progress towards an activator-free single-component catalytic system for α-olefin polymerization using group 4 metal catalysts having tridentate "LX_2" ligands with phenolate arms on N-heterocyclic carbene L donors. We have designed a new tridentate dianionic anilide-pyridine-phenoxide (NNO) ligand to support group 4 metals for olefin polymerization. Unexpectedly, the Ti catalyst system polymerizes propylene in a nearly regio-random fashion, an unprecedented behavior for an early transition metal system. We have identified a Zr(III) component as a significant component of a propylene polymerization system formed from a zirconocene dichloride, di(isobutyl)aluminum hydride and trityl tetra(pentafluorophenyl)borate. This NMR-silent component is in accord with earlier observations from our group and others that rough half of the zirconium species are inactive during polymerization of propylene.

Controlling Selectivity of Heterogeneous Catalysts Using Grafted Metallocalixarene Active Sites

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Students: 1 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding: $150,000

PROGRAM SCOPE

This program aims to synthesize open coordination sites for catalysis when using grafted metal cations on inorganic oxide surfaces. The approach uses design and synthesis of well-defined, isolated, supported molecular catalyst active sites consisting of grafted metallocalixarene complexes; characterization relies on 13C CP/MAS NMR, FTIR, and DR-UV-Vis spectroscopies. A goal of the program is to demonstrate new methods for control of catalytic activity and selectivity on surfaces by virtue of tunability of the organic ligand, with an emphasis on the comparative synthesis and characterization of open and closed grafted metal cation sites.

FY 2012 HIGHLIGHTS

We have demonstrated the first well-defined open and closed grafted metal cation sites on an inorganic oxide (in press in Proceedings of the National Academy of Sciences USA). These sites consist of Al(III)-calixarene complexes grafted on the surface of silica. Using this ability, we have provided one of the rare demonstrations of kinetic consequences of open and closed sites for oxo-transfer catalysis consisting of olefin epoxidation using organic hydroperoxide as oxidant. Both open and closed variants of the active site were shown to be equally active, and this was consistent with predictions using molecular modeling (DFT-based) calculations. In contrast, for hydride transfer catalysis consisting of the MPVO reaction, only the open variant of the site was active. These data answer longstanding questions about open/closed connectivity requirements for epoxidation, and more generally, demonstrate control of reactivity using metal cations on surfaces using an open/closed approach that is enforced by a permanently bound organic ligand.

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

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Funding: $300,000

PROGRAM SCOPE

To understand the class of metal cluster catalysts better 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 being 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 state-of-the art spectroscopic, microscopic, and computational methods to determine their structures, reactivities, and catalytic properties. The ligands range from nearly flat MgO surfaces to enveloping zeolites to bulky calixarenes to provide controlled coverages of the metal clusters. With this wide range of ligand properties and our arsenal of characterization tools, 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 using methods of organometallic and inorganic chemistry combined with surface chemistry for the precise synthesis of metal clusters and nanoparticles, characterizing them at various stages of preparation and under various conditions (including catalytic reaction conditions) and determining their structures and reactivities and how their catalytic properties depend on their compositions and structures.

FY 2012 HIGHLIGHTS

- When synthesizing coordinatively unsaturated (decarbonylated) clusters of the family $Ir_4(CO)_X(phosphine)_{12-X}$, we observed a preferential ability to stabilize the cluster in a decarbonylated state when using large ligands such as calixarene phosphines relative to the isoelectronic but slightly smaller $MeP(Ph)_2$. Thus a focus of our ongoing efforts is to understand how large ligands can be used to stabilize coordinatively unsaturated sites in metal clusters.
- We have used computational chemistry to predict the reaction chemistry of a family of iridium clusters of the family $Ir_n(CO)_m$, including exothermicity of the nucleation reactions when CCSD(T) calculations are infeasible. These results are linking experiments such as those mentioned above with calculated results.
- We observed the first stages of metal cluster formation, using aberration-corrected STEM to image individual Ir atoms in the straight, nonintersecting pores of the zeolite SSZ-53.
- We found that sintering of iridium clusters on supports stops at a critical diameter of approximately 1 nm with clusters of this size bouncing off each other; this “smart” catalyst is intrinsically sinter resistant.
- We have reported extensive calculations characterizing complexes and small clusters of Co, Rh, and Ir on supports, finding good agreement with experimental spectra.
- We recorded the first tomographic images of a delaminated zeolite, determining its three-dimensional structure and porosity in unprecedented detail and gaining insight into the process of delamination.
- We used STEM to determine three-dimensional structures of small osmium clusters on MgO.

Tailoring Supports as Ligands: Zeolites and Oxides as Hosts of Molecular Metal-Complex Catalysts

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Funding:	$200,000

PROGRAM SCOPE

The simplest supported metal catalysts, like the simplest organometallic catalysts in solution, consist of single metal atoms stabilized by ligands. The supports are ligands. Our focus is on precise synthesis of such supported catalysts, with the metals being noble—because of their wide applications in catalysis—and the supports being crystalline—because their well-defined structures facilitate fundamental understanding of the catalytic species on them. 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. Also we have learned how to make a catalyst with properties superior to those of any reported for selective hydrogenation of 1,3-butadiene.

The supports are primarily 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 the supported catalysts. We believe that the understanding emerging from 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.

FY 2012 HIGHLIGHTS

- We used scanning transmission electron microscopy to resolve individual atoms of Ir, Os, and Au on zeolite and MgO supports.
- The site-isolated gold cations are identified as catalytic sites for CO oxidation; these constitute the best-defined supported gold catalyst.
- A new mechanism was discovered for olefin oligomerization in the absence of halides; it involves a rhodium complex and OH groups on an acidic support.
- We prepared well-defined zeolite- and MgO-supported iridium and supported rhodium complexes, varied the ligands on the metal, characterized the samples with IR and EXAFS spectroscopies, and resolved the effects of the supports, the other ligands, and the metal nuclearity on the activity of the catalyst for ethylene hydrogenation and for H-D exchange in the reaction of $H_2 + D_2$.
- We demonstrated how to switch the selectivity of a supported catalyst by variation of the reactant gas composition; the selectivity switch results from a switch of the rhodium in the catalyst between isolated mononuclear complexes and small rhodium clusters.
- We designed a catalyst for selective hydrogenation of 1,3-butadiene to give butenes; it is characterized by better activity and selectivity than any reported.
- Maria Flytzani-Stephanopoulos and the PI wrote a critical review of atomically dispersed supported metal catalysts.

Advancing Chemistry with F Elements

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Students: 0 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding: $125,000

PROGRAM SCOPE

The objective of this research is to use the unique chemistry available from complexes of the lanthanides and actinides, as well as related heavy metals such as scandium, yttrium, and bismuth, to advance chemistry in energy-related areas. The lanthanides and actinides have a combination of properties in terms of size, charge, electropositive character, and f valence orbitals that provides special opportunities to probe reactivity and catalysis in ways not possible with the other metals in the periodic table. We seek to discover reaction pathways and structural types that reveal new options in reaction chemistry related to energy. Identification of new paradigms in structure and reactivity should stimulate efforts to develop new types of catalytic processes that, at present, are not under consideration because either the transformation or the necessary intermediates are unknown. Activation of normally unreactive C-H bonds in the methyl groups of pentamethylcyclopentadienyl ligands, $(C_5Me_5)^{1-}$ to form complexes of tuck-over ligands, $(\mu\text{-}\eta^1{:}\eta^5\text{-}CH_2C_5Me_4)^{2-}$, is one area that is targeted for this approach.

FY 2012 HIGHLIGHTS

The reactivity of the tuck-over hydride complex, $(C_5Me_5)_2Y(\mu\text{-}H)(\mu\text{-}\eta^1{:}\eta^5\text{-}CH_2C_5Me_4)Y(C_5Me_5)$, made by C-H bond activation has been studied. The complex can effect unexpected two electron reduction chemistry as well as stepwise sigma bond metathesis. The complex allowed direct comparison of Y-C versus Y-H bond reactivity within a single complex. Higher reactivity was observed for the hydride ligand. These results also show that such bimetallic tuckover hydride species can engage in reactions appropriate for making useful comparisons between two different metals in mixed metal analogs. The reaction of the mixed metal tuckover hydride, $(C_5Me_5)_2La(\mu\text{-}H)(\mu\text{-}\eta^1{:}\eta^5\text{-}CH_2C_5Me_4)Y(C_5Me_5)$, with PhSSPh to form $[(C_5Me_5)_2Y(\mu\text{-}SPh)_2La(C_5Me_5)(\mu\text{-}SPh)]_2$ is an example.

C-H bond activation has also been explored with bismuth, the metal used in the SOHIO process. The chemistry of the new dianionic ligand, $[C_6H_2(t\text{-}Bu)_2O]^{2-}$, an oxyaryl moiety formed by facile C-H activation from a bismuth phenoxide, is being developed through reactivity studies and comparisons with the oxyarylcarboxy derivative, $[O_2CC_6H_2(t\text{-}Bu)_2O]^{2-}$, formed by the first insertion of CO_2 into a bismuth-carbon bond. A cyclic process catalytic in bismuth has been identified for converting phenoxides to silyl ethers.

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

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Students:	1 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$120,000

PROGRAM SCOPE

The reactive behavior of individual molecules is seldom observed because we usually measure the average properties of billions of molecules. What we miss is important; the catalytic activity of less than 1% of the molecules under observation can dominate the outcome of a chemical reaction seen at a macroscopic level. The goals and objectives of this program are to (1) image individual steps in organic, organometallic, and inorganic reaction mechanisms using single-molecule fluorescence microscopy and (2) use this increased understanding to develop new catalytic reactions.

FY 2012 HIGHLIGHTS

We successfully detected the dimerization of individual polymer strands under catalytic conditions with Grubbs' catalyst. In addition, we used bright-field microscopy to image the catalytic polymerization of ethylene oxide on the surface of a cobalt-salph catalyst. These results established the feasibility of a heterogeneous polymerization pathway for this catalyst. In the next period, we envision probing the crystal-face selectivity of the location for polymerization initiation. Through this study, we aim to build a structure/function relationship that aids in understanding the mechanism of polymerization.

Design and Characterization of Novel Photocatalysts with Core-Shell Nanostructures

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Funding:	$380,000

PROGRAM SCOPE

The overall goal of this project is to develop new photocatalysts that use light to produce hydrogen from water. Specifically, we aim to develop a new and novel class of well-characterized nanostructured Metal/TiO_2 core-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 H_2 and O_2 on the metal surface once produced. In the first years of this project, we established the synthetic parameters for full control of the synthesis of our original yolk-shell architecture and developed the tools to characterize those catalysts. In terms of the synthesis, we aimed at independently controlling the size and nature (Au, Pt) of the metal nanoparticles in the core and the overall diameter, thickness, and crystalline structure of the titania shells. Regarding the characterization of the samples, diffuse-reflectance infrared absorption spectroscopy has been fully implemented to evaluate the capacity of both the metal and the oxide to uptake probe molecules such as CO as a function of temperature and time, in order to evaluate the diffusivity of gases through the shells and measure simple catalytic oxidation reactions. Time-resolved measurements were also implemented to follow the electronic transitions involved in the photon excitation, electron transfer, and electron-hole pair recombination processes.

FY 2012 HIGHLIGHTS

We have made advances in each of the specific objectives listed above. From a synthetic point of view, we have extended the original yolk-shell design to create a sandwich structure, synthesized by a combination of nonmetal doping and plasmonic metal decoration of TiO_2 nanocrystals, to improve visible-light activity and to enhance light harvesting and charge separation, respectively. We also developed a method for the control of the nanoscale crystallinity in mesoporous TiO_2 shells. In terms of the performance of these catalysts, a novel in-situ IR titration method was developed to assess the degree of diffusion through the shells of yolk-shell and core-shell nanostructures made in this project in the liquid phase. Finally, a correlation was identified between the excited state relaxation dynamics of Au/TiO_2 core-shell nanostructures, measured by photoluminescence and transient absorption, and their photocatalytic activity.

Transition-Metal-Catalyzed Hydroamination of Non-Activated Carbon-Carbon Multiple Bonds with Ammonia

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Funding:	$155,000

PROGRAM SCOPE

The goal of this project is the development of efficient homogeneous catalysts allowing for the Markovnikov and anti-Markovnikov hydroamination of unactivated carbon-carbon multiple bonds with ammonia. 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 as the amine partner. 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.

FY 2012 HIGHLIGHTS

The difficulty associated with the use of NH_3 for homogeneous catalysts is mainly due to the formation of stable Lewis acid-base complexes, the so-called Werner complexes. To achieve our goal, it is necessary to design ligands, which transform Werner complexes into reactive species. In 2012, we have reported the preparation of cyclic diaminocarbenes with a pyramidalized nitrogen atom (Angew. Chem. Int. Ed. 2012, 51, 6172-6175). These ligands feature enhanced electrophilicity compared to classical NHCs.

We have also reported the synthesis of a phosphinonitrene, which is the first non-metallic nitrene that is stable at room temperature in solution; it can even be isolated in the solid state (Science 2012, 337, 1526-1528). The bonding between phosphorus and nitrogen is analogous to that observed for metallonitrenes, which are important intermediates in biological nitrogen fixation by the nitrogenase enzymes, and the industrial Haber-Bosch hydrogenation of N_2 into NH_3. We have shown that this nitrido phosphorus derivative can be used to transfer a nitrogen atom to organic fragments, a difficult task for transition metal nitrido complexes.

Transition-Metal-Catalyzed Hydroamination of Non-Activated Carbon-Carbon Multiple Bonds with Ammonia

Institution:	California-Riverside, University of
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Students:	2 Postdoctoral Fellow(s), 0 Graduate(s), 1 Undergraduate(s)
Funding:	$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

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FY 2012 HIGHLIGHTS

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Int. Ed. 2012, *51*, 6172-6175). These ligands feature enhanced electrophilicity compared to classical NHCs.

We have also reported the synthesis of a phosphinonitrene, which is the first non-metallic nitrene that is stable at room temperature in solution; it can even be isolated in the solid state (Science 2012, *337*, 1526-1528). The bonding between phosphorus and nitrogen is analogous to that observed for metallonitrenes, which are important intermediates in biological nitrogen fixation by the nitrogenase enzymes, and the industrial Haber-Bosch hydrogenation of N_2 into NH_3. We have shown that this nitrido phosphorus derivative can be used to transfer a nitrogen atom to organic fragments, a difficult task for transition metal nitrido complexes.

Bond-Formation and Catalysis by Base-Metal Unsaturated Isocyanides

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Funding:	$150,000

PROGRAM SCOPE

The goal of this project is to use the inexpensive, middle 3d-transition metals (base metals) manganese and cobalt as high-efficiency reagents and catalysts for chemical-bond formation. A specific aim of this proposal is the development and mechanistic elucidation of manganese-based electrocatalysts for carbon dioxide (CO_2) reduction and fixation. Efficient activation and recycling of atmospheric CO_2 remains a significant contemporary challenge as global demand for carbon-based fuel sources continues to increase. Experiments and studies of this project focus specifically on the development and mechanistic elucidation of a new, manganese-based system for electrochemical reduction of carbon dioxide to water and carbon monoxide (CO). The new manganese catalysts proposed here feature *m*-terphenyl isocyanides as supporting groups. These isocyanides and their transition metal complexes represent a new class of molecular species that are inspired from classic, binary transition-metal carbonyls, which are themselves catalysts for important chemical transformations. The *m*-terphenyl isocyanide complexes studied in this project offer a robust, but highly modular, platform for electrocatalyst development and optimization. Such ligand-directed control is lacking in metal carbonyl systems. In addition, the protective and tunable nature of *m*-terphenyl isocyanides allow for detailed assessment of the elementary steps operative in CO_2 reduction processes. The second aim of this proposal concerns the discovery and elucidation of new bond formation processes using cobalt isocyanide-containing molecules. This work seeks to significantly advance the chemistry available to recently discovered cobalt *m*-terphenyl isocyanide complexes of unique construction and properties, especially as applied to CO_2 remediation.

FY 2012 HIGHLIGHTS

Since May 2012, we have made good progress toward the synthesis and/or study of two distinct isocyanide systems for CO_2 activation. We have conducted the preliminary synthetic and chemical reduction studies of three new isocyanide supported Mn-systems and have determined their propensity to interact with CO_2. We have also explored the decarbonylation chemistry of CO_2 with our targeted cobalt isocyanide complex. In the next phase of the project, we will determine the electrocatalytic behavior of the Mn-based system and further elucidate the mechanism of CO_2 activation in our Co-based isocyanides.

Hierarchical Design of Supported Organometallic Catalysis for Hydrocarbon Transformations: Structures and Dynamics of Active Sites

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Funding:	$540,000

PROGRAM SCOPE

The application of surface organometallic chemistry and spectroscopic characterization methods to catalyst development promises to bring a new level of molecular understanding, and molecular-level control, of active site structure and reactivity in heterogeneous catalysis. At the same time, a deeper appreciation of the role of the support oxide in activating the supported organometallic fragment is required in order to be able to use this understanding to design new heterogeneous catalysts. This collaborative project brings together expertise in organometallic chemistry, surface science, sol-gel synthesis, x-ray absorption spectroscopy and magnetic resonance methods for the characterization of materials and catalysts, as well as computational modeling of reaction intermediates and pathways, in order to create a complete picture of the activation, deactivation, and reactivation of supported organometallic catalysts. The project specifically targets the development of new, robust catalysts that activate spontaneously in the presence of a hydrocarbon substrate. Hydrocarbons are the foundation of the chemical feedstock value chain, and these reactions were chosen specifically for their high potential for immediate and long-term impacts on chemical manufacturing, as well as their general importance for advancing fundamental understanding of catalytic processes. Metal oxides must form metal-carbon bonds in order to perform many of these transformations, but the mechanisms and efficiencies of these key initiating steps remain unknown. Many catalytic processes suffer from a low fraction of active sites and a rapid rate of deactivation, with poor tolerance of substrate functionality. Through understanding of the molecular nature of the active sites and their reactivity, we aim to increase active site fractions, enhance tolerance of polar and protic molecules, and decrease rates of deactivation.

FY 2012 HIGHLIGHTS

Ab initio modeling of reactivity in catalysts based on amorphous materials is particularly difficult because of the problems presented by ill-defined structural heterogeneity. Crystalline models are incapable of accurately representing the reactivity of such systems. We have reduced the high dimensional space of active site structures, each with different reactivities, to a sequence of representative low energy sites with activation energy itself as the sequence ordering parameter. Such a calculation would require prohibitively costly nested constrained optimizations, but a sequential quadratic programming formulation generates the range of sites efficiently and without ad hoc structural assumptions. Once generated in this systematic manner, the structures of “dead” and “active” sites can be compared to understand structure-property relationships for catalysis on amorphous surfaces. This approach is being tested in the modeling of active sites for supported olefin metathesis and polymerization, using compositional and structural information derived from well-defined surface organometallic complexes.

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

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Funding:	$160,000

PROGRAM SCOPE

The aim of this project is to improve our understanding of catalysis with doped metal oxides for C-H bond activation and transformations of light alkanes by establishing a correlation between experimentally observed performance trends and mechanistic predictions supported by density functional theory. The research probes the fundamental relationships between surface chemistry and the electronic structure of the catalyst surface as well developing and proving new catalyst synthesis techniques. Our goal is to design better catalysts for important reactions of methane, ethane, and propane. Transformation of light hydrocarbons by heterogeneous catalysis is extensively used in industry and has a direct impact on the global economy. Catalysts that selectively activate C-H bonds without activating C-C bonds are of interest in many chemical processes that require carbon chain length integrity and involve selective activation of C-H bonds. Thus far, we have shown how doped oxides can be prepared with high activity for methane “dry reforming” with carbon dioxide and how to favor partial oxidation to syngas over complete oxidation to carbon dioxide. We have also demonstrated oxidative dehydrogenation of C2+ alkanes including propane as model reactant to generate propylene and synthesis gas by using various doped metal oxide catalysts at low temperature. The program also seeks to make more efficient use of carbon dioxide as the oxidant to increase the propylene yield using novel and selective doped oxide catalysts.

FY 2012 HIGHLIGHTS

Various doped metal oxide catalysts (e.g., Ru, Cr doped in CeO_2, ZrO_2, or SiO_2) have been synthesized successfully and studied for oxidation of propane at low temperatures. To compensate for lower equilibrium conversion at lower temperatures, carbon dioxide is co-fed to increase the conversion by reacting with hydrogen pulling the propane-propylene equilibrium to the right. In the conversion of propane over Ru doped catalysts, the major products are CO and H_2. The catalyst has also been successful in methanation, which is of interest to convert C2+ alkanes into methane for use in existing natural gas transportation infrastructure. Additionally, several dopants in lanthanum oxide have been investigated experimentally and theoretically and a strong correlation discovered between methane effective activation energies and DFT-calculated oxygen vacancy energies. The activity of Ru doped CeO_2 is higher than Ru doped ZrO_2 for the C-C cleavage producing higher yields of CO and H_2. This is a promising route for the low temperature production of synthesis gas. CO_2 facilitates the catalytic reactivity and increases the yield, and we are evaluating the role of surface carbonate species. Chromium doped silica has recently been shown to have a high selectivity at low temperatures for oxidative dehydrogenation of propane with CO_2. Optimization of this catalyst is in progress.

We are also studying an " inverse" catalyst, metal oxide-on-metal which has oxide-metal boundaries that give high catalytic activities. Such systems are a promising platform to study the microscopic mechanism of catalytic process during chemical reactions. We are studying the catalytic processes of VO_x clusters on Au (111) and Ag (111) surfaces, with the focus on methane dehydrogenation. In a catalytic oxidation cycle, VO_x is firstly reduced and then reoxidized, or vice versa. By calculating the lowest energy structure of various VO_x (x = 1-5) clusters supported on metal and the Bader charge on the vanadium atom, we study the stoichiometry and the structures of the reduced and oxidized forms of vanadia that can be involved in catalytic reactions.

Platinum Group Metal (PGM) Substituted Complex Oxide Catalysts: Design of Robust Materials for Energy-Related Redox Transformations

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PROGRAM SCOPE

The increasing costs of platinum group metals (PGMs), arising from their scarcity and ever-growing use in catalytic converters, provide the imperative for research into better use of PGMs in catalysis. A significant body of recent work, including from Santa Barbara and elsewhere, has pointed to the effectiveness of complex transition metal oxides substituted with small amounts of noble metal ions (notably, Pd^{2+}) in oxidation catalysis. This area of research has yielded a number of important surprises, chief amongst which is the increasing body of evidence pointing to Pd^{2+} in the oxide lattice, rather than Pd nanoparticles on the surface of the oxide, that are the active sites for CO oxidation. This has led us to question the paradigm of oxide-supported PGM nanoparticle catalysis—at least for a large class of important oxidation and partial oxidation reactions—and to envisage the development of catalysts that obviate problems inherent to supported catalysts, such as inefficiencies due to only surface atoms being accessible, particle sintering with concurrent loss of active surface area, and ablation. Specific goals include continuing to build a body of evidence pointing to the role that the substituted PGM ions in the oxide host play in catalytic oxidation, extending our exploration to other PGM systems as well, including Rh^{3+} and Pt^{4+}, and developing model Pd^{2+} and Au^{3+}, Rh^{3+}, and Pt^{4+} oxides (e.g., Y_2BaPdO_5, La_4LiAuO_8, $LaRhO_3$, and Ba_2CePtO_6) and using them to shed light on the burning question regarding active sites: metal ion or nanoparticle?

FY 2012 HIGHLIGHTS

We have investigated Pd-substituted CeO_2. This substituted simple oxide has been well-studied for use in CO oxidation and NO_x reduction, and the water-gas shift reaction. We have investigated this compound, prepared by ultrasonic spray pyrolysis, for partial oxidation and dry-reforming of CH_4. We have also, in this period, completed our comprehensive study of the electronic structure of gold compounds, in the search for new catalytic materials where the active element is gold. In this light, and as a precursor to further experiments, we also examine the chemistry of Ir^{4+} and a specific case of a Pd^{2+} compound using first-principles electronic structure calculations.

Atomically Precise Metal Nanoclusters for Catalytic Application

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PROGRAM SCOPE

The goal of this project is to correlate the catalytic properties of atomically precise metal nanoparticles (e.g., Au, Ag) with their atomic structure. Such correlation will ultimately unravel some fundamental aspects of nanocatalysis, such as the nature of particle size effect, particle-support interactions, the identification of catalytically active centers, etc. We have successfully prepared different sized, robust gold nanoclusters protected by thiols, such as $Au_{20}(SR)_{16}$, $Au_{25}(SR)_{18}$, $Au_{38}(SR)_{24}$, $Au_{40}(SR)_{24}$, $Au_{55}(SR)_{31}$, and $Au_{144}(SR)_{60}$, etc. All these ultrasmall nanoclusters (< 2 nm) exhibit discrete electronic structure due to quantum size effect (as opposed to quasicontinueous band structure of conventional metal nanoparticles or bulk metals). Among the gold nanoclusters, $Au_{25}(SR)_{18}$ and $Au_{38}(SR)_{24}$ have been crystallographically characterized. Significantly, Au_{38} possess a chiral structure, which will allow us to investigate enantioselective catalysis (e.g., hydrogenation) based on intrinsically chiral nanoclusters (rather than chiral ligand-modified metal surfaces). We will also investigate the selective oxidation reactions and the O_2 activation mechanism on nanocluster catalysts. Hetereoatom-doped nanoclusters will be compared with homogold nanocluster catalysts to probe the effect of single doping atom (e.g., Pt, Pd). Other specific aims include nanocluster-support interactions and the effect of ligands. Overall, atomically precise metal nanoclusters constitute a new class of materials and will offer some exciting opportunities for fundamental catalysis and other energy-related research. These well-defined nanocatalysts are expected to mediate the knowledge gap between single crystal model catalysts and real-world conventional nanocatalysts. Correlation between the crystal structures of nanoclusters and their catalytic properties will ultimately permit a deep understanding of the origin of nanocatalysis and many fundamentally important questions. Such knowledge will provide important guidelines for the future design of new catalysts with high selectivity, activity, and durability for some chemical processes.

Early Career: Multifunctional Oxygen Evolution Electrocatalyst Design and Synthesis

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PROGRAM SCOPE

Oxygen plays a crucial role in determining the efficiency of many energy technologies. For example, in water electrolysis, oxygen is a byproduct in the production of hydrogen, yet it is the efficiency of the oxygen evolution reaction that determines the efficiency of the whole operation. The oxygen evolution mechanism is complex, and it is likely that the electrocatalyst will have to be multifunctional to effectively catalyze multiple steps in the mechanism. At a scale that is relevant for energy applications, oxygen evolution catalysts must be cheap, active, and stable. Oxide-based materials are one of the most promising materials for oxygen evolution electrocatalysis that has already been established in large-scale industrial applications. We use an integrated approach combining computational, basic, and applied science to identify the essential, rate limiting steps in the oxygen evolution mechanism on cost-effective oxide-based materials, and to develop new approaches to promoting these materials to make them more active.

We will investigate the promotion of nickel oxide based electrocatalysts for oxygen evolution with other transition metal oxides. In the first computational stage, we utilize an electrochemical atomistic thermodynamic framework based on density functional theory calculations to assess the stability of nickel oxide surfaces under electrochemical conditions appropriate for oxygen evolution. We use density functional theory to develop a baseline reaction energy profile for a prototype mechanism of oxygen evolution on nickel oxide. We then use density functional theory to screen the stability and activity of base transition metal promoters in nickel oxide for the oxygen evolution reaction, including the diffusion of reactive intermediates between the promoting sites and the nickel oxide sites. In parallel, we perform in situ Raman spectroscopic and synchrotron studies under oxygen evolution conditions to determine the nature of the active surface under reaction conditions.

FY 2012 HIGHLIGHTS

The PI was awarded a Presidential Early Career Award for Scientists and Engineers. We published one paper identifying a potential mechanism of the Fe-promotion of nickel oxide as an oxygen evolution electrocatalyst via the formation of a new spinel phase. One graduate student supported by this work graduated, and a new student began working on the project. The new student is developing approaches to incorporate advanced electronic structure methods such as DFT+U and hybrid functionals into modeling the oxygen evolution reaction on Ni and Fe-oxide based surfaces.

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

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Funding:	$640,000

PROGRAM SCOPE

In this project, we are guided by the idea 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. We consider the dynamics of reactants as they undergo chemical transformation at the active sites of a heterogeneous catalyst and highlight the importance of the constant structural (e.g., morphology, density, and nature of surface defect sites) and chemical (e.g., oxidation state of surface atoms and variation in the composition of the surface layer) reorganization during the course of a chemical process in a reactive environment. In addition, we pursue the idea 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.

FY 2012 HIGHLIGHTS

We have investigated the properties of MoS_2 as a function of layer thickness using a wide range of experimental and theoretical techniques. We have also established a novel method for preparing monolayer MoS2 on a Cu(111). Experimental investigation and theoretical modeling of the Moiré patterns exhibited by the films indicate that the underlying copper surface is free of sulfur. The S-Mo-S triple layer rests on a (111) terminated copper substrate, without the presence of additional sulfur. Theoretical modeling shows a slight buckling of the underlying substrate and presence of two different registries of the film on the substrate. In addition to aligned MoS_2 films and islands, we find on our sample two other distinctive MoSx-based morphologies, whose structure and properties we investigated: Mo_6S_6 nanowires and a Mo_2S_3 film. DFT based modeling was a key to understanding these structures and establishing their characteristics.

Our project has made significant progress in understanding reactant transport at surfaces through application of novel theoretical methods and through experiments that offer precise imaging or spectroscopic resolution of reactant dynamics. We have obtained both experimental and theoretical data on the rearrangement of the catalyst during reaction and how such processes are affected by the presence of reactants. Originally working predominantly on metal substrates, we have devised methods for simulating complex catalyst while maintaining the atomic scale focus that is fundamental to our approach. We have developed theoretical methods to investigate reaction prefactors, reaction rates, and dispersive, non-local interaction. In the choice of the catalytic reactions, we continue juxtaposing conventional heterogeneous catalytic processes with emerging ones, for instance addressing on the one hand CO and methanol oxidation at bimetallic particles on chalcogenide (including oxide) support, and on the other hand the synthesis of MoS_2 and grapheme on copper.

Size- and Shape-Selected Micellar Metal Nanoparticles as Model Systems for Structure-Sensitive Chemical Reactions: Oxidation State Effects

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PROGRAM SCOPE

Unraveling the complex interaction between catalysts and reactants under operando conditions and tailoring their chemical reactivity at the atomic level are key steps towards gaining fundamental insight in catalysis. This project contributes to improving the present understanding of the mechanisms underlying the distinct activity, selectivity, and stability of metal nanoparticles (NPs) supported on oxides used in industrially relevant chemical reactions including CH_4, CO, CO_2, and alcohol conversion. Size- and shape-selected micelle-synthesized NP catalysts are being employed to study the interaction of nanoscale metal surfaces with oxygen, and to identify the active sites (metallic, oxidized, or metallic with dissociatively-chemisorbed oxygen) under reaction conditions. Such knowledge will be used to optimize the nanocatalyst's structure and to select the oxide support and secondary metal in bimetallic systems, since all of these aspects influence the oxidation state of the NP catalysts and their catalytic performance.

The selective conversion of methane, carbon monoxide, and carbon dioxide to commercially valuable chemicals and liquid fuels (methanol) is of substantial societal and industrial interest, since these are the main gases responsible for the greenhouse effect.

FY 2012 HIGHLIGHTS

The enhanced thermal stability of micellar Pt NPs and the importance of the sample pre-treatment and annealing environment in the minimization of undesired sintering processes affecting the performance of nanosized catalysts was demonstrated. In particular, annealing pre-treatments in pure oxygen were found to contribute to the stabilization of Pt NPs on γ-Al_2O_3. Our data suggest that PtOx species, possibly modifying the NP/support interface, play a key role in the stabilization of small metal NPs.

The chemisorption of oxygen and subsequent oxidation of size-selected Pt NPs supported on C was investigated in situ in an electrochemical environment. Lower onset potentials for oxidation and stronger Pt-O binding were observed for the NP samples as compared to bulk Pt(111).

The chemical state of Pt NPs supported on γ-Al_2O_3 was investigated under methanol oxidation reaction conditions. Reactivity measurements following oxidative and reductive pretreatments show clear differences at low temperature, with an enhanced reactivity of the oxidized NPs. For the pre-reduced catalysts, the metallic NPs are also partially oxidized upon exposure to the reactants, but with a different structure that makes them less active and less stable than what is formed in the oxidative pretreatment.

Cu, Pd, and Cu-Pd NPs supported on γ-Al_2O_3 were studied during the catalytic hydrogenation of CO to methanol. The presence of Pd in the bimetallic Cu-Pd NPs results in the stabilization of the nanocatalysts against sintering at 360˚C and 15 bar. The formation of Cu-Pd bonds was observed in our extended x-ray absorption fine-structure spectroscopy measurements, indicating our micelle-based synthesis can be successfully used for the production of bimetallic Cu-Pd catalysts with narrow size distributions.

Surface Termination of M1 Phase and Rational Design of Propane Ammoxidation Catalysts

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PROGRAM SCOPE

This research program is focused on studying the nature of X substitution (X=Ta, Nb and Sb) in the M1 structure for different synthesis X/Mo ratios, their impact on the Mo/V distribution at the proposed active center present in the surface *ab* planes, topmost surface composition, and the catalytic behavior of resulting M1 phases in order to build more accurate fundamental relationships between the molecular structure and catalytic behavior of the surface *ab* planes of the M1 catalysts in propane ammoxidation. It will also focus on elucidating the bulk microstructures, topmost surface compositions, the catalytic role of the M2 phase, and the nature of synergy between the M1 and M2 phases.

The fundamental insights gained in these studies will enable construction of improved models of the M1 and M2 active surfaces for theoretical studies of propane ammoxidation that will examine how various surface metal oxide species influence elementary steps of propane ammoxidation, e.g., propane activation, α-H abstraction from the propylene intermediate, and the NH insertion into the π-allylic surface intermediate to form acrylontrile. Lastly, fundamentally-based microkinetic modeling will be performed in order to pull this information together for the purpose of both understanding and prediction.

FY 2012 HIGHLIGHTS

Theoretical (DFT) and experimental approaches (STEM) employed to probe Ta locations in the Ta-substituted M1 phase used a model for the structurally, chemically, and catalytically similar Nb-M1. This research established, for the very first time, that Ta is present only in site 9 and is distributed uniformly throughout the M1 lattice. A clear correlation between the Ta partial occupancy of site 9 and the acrylonitrile yield was demonstrated, providing, for the very first time, direct evidence of the active site isolation phenomenon proposed earlier. Given its success, DFT was applied to Nb-M1, where Nb and Mo locations could not be distinguished experimentally, and it confirmed, for the very first time, that Nb is also located predominantly in site 9.

The cluster models of the M1 phase containing Nb in site 9 were employed in DFT studies of propane ammoxidation, which revealed a linear correlation between the H absorption energy and transition state energy during C-H bond activation in propane. This correlation serves as a reliable predictor of activity, which correctly predicted very low catalytic activity of the Nb=O species in site 9 and much lower activity of V(IV) than V(V) in C-H bond activation in propane. Further DFT studies revealed that i-propyl and allyl radicals prefer to adsorb on Te=O and V=O, and that Mo=O is the preferred site for ammonia adsorption and activation into imido species. The latter species have been confirmed by DFT as the active sites for the imido group insertion into the allyl radicals, which occurs essentially without an energy barrier.

Catalyic Conversion of Glucose and Cellulose into HMF: From a Fundamental Understanding to Discrete and Recyclable Catalyst Discovery

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PROGRAM SCOPE

The overall objective of this project is to seek a fundamental understanding of the catalytic cellulosic biomass conversion into the platform chemical 5-hydroxymethylfurfural (HMF), under mild and homogeneous conditions, and apply the knowledge gained from this study to develop more efficient, selective, environmentally friendly, and cost-effective biomass conversion processes.

This project is built upon a recent discovery in the PI’s lab that cellulose dissolved in certain ionic liquids (ILs) is effectively deconstructed under mild conditions, without addition of mineral acids typically employed in cellulose conversion systems, into water-soluble reducing sugars in near quantitative yield. Furthermore, the resulting reducing sugars, or their precursory cellulose, are readily converted into HMF in high conversion with a metal halide catalyst in ILs. These exciting preliminary results, in essence, solved a recognized issue with acid catalysts used in cellulose hydrolysis by realizing the unique triple roles of the IL/H_2O mixture. However, three other challenges in the glucose- and cellulose-to-HMF conversion process are still unmet: (1) there lacks a fundamental understanding of the mechanism involved in such conversions, (2) it requires a high loading of the relative expensive and toxic chromium chloride catalyst, and (3) it requires the use of expensive IL solvents.

Accordingly, the proposed research employs the experimental methods, including techniques for mechanistic, structural, and synthetic studies of catalysis as well as for polymer and nanoscale science methods, to accomplish the following four specific objectives: (1) understand how glucose is converted into HMF in organic and IL solvents, (2) develop discrete molecular and metal complex catalysts for the selective glucose-to-HMF conversion, (3) understand how cellulose solubilized in ILs is converted into HMF in the presence of discrete catalysts, and (4) develop polymeric ILs (PILs) and recyclable PIL-supported metal catalysts for greener and cost-effective biomass conversion into HMF.

FY 2012 HIGHLIGHTS

We have successfully developed several new catalyst systems for effective conversion of glucose or cellulose into HMF, including catalysts based on inexpensive aluminum alkyls and alkoxides, highly reactive metal(0) nanoparticles, and recyclable polymeric ionic liquid supported metal complexes.

Supported-Nanocluster Catalyst Formation Kinetic and Mechanistic Fundamental Studies

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PROGRAM SCOPE

The primary objective of this project is to follow the kinetics and establish the mechanism(s) of the nucleation and growth of supported-nanocluster heterogeneous catalysts. Heterogeneous catalysts are a crucial class of industrial catalysts which make a multitude of products underpinning modern society. However, the detailed chemical events of how they form, and therefore how to better control that formation and hence their overall synthesis and resultant catalytic properties, remains an important, unsolved problem. A broader goal of the research is to learn how to best transfer the synthetic and mechanistic insights, from the modern revolution in nanoparticle synthesis and characterization in solution, to the preparation of the next generation of supported-nanoparticle heterogeneous catalysts—again with the goal of improving those catalysts for the production of chemical products important to modern society. Four specific aims are being addressed en route to answering the question of how the recently developed prototype system of oxide-supported $[(1,5\text{-COD})IrCl]_2/\gamma\text{-}Al_2O_3$ evolves into a high-activity, long lifetime oxide-supported $Ir(0)_n$ catalyst. Another key question being addressed is what variable(s) lead to the greatest, mechanism-based particle-size control—that size control being central to the efficiency and chemical selectivity of the resultant catalysts. Experiments probing how the resultant catalysts perform in classic chemical reaction tests of size-varied catalysts, that is, in so-called structure-insensitive and structure-sensitive reactions, round out the approach and methods being utilized.

FY 2012 HIGHLIGHTS

Seven publications resulted from our DOE-supported research. A review titled “A Review of the Kinetics and Mechanisms of Formation of Supported-Nanoparticle Heterogeneous Catalysts” was published that details what is, and is not, known about the mechanisms of supported nanoparticle formation—an important step towards advancing the science in this area. In a second important paper, experimental evidence was published revealing that the crucial nucleation step in nanoparticle formation is a simple bimolecular process, that nucleation step being significant in that it starts—and thereby exerts significant control over—the whole supported-nanoparticle formation process. Additional publications resulted addressing (1) when small, sub-nanometer, M_4 (M = transition-metal) clusters are formed instead of larger, M_n nanoclusters; (2) how catalyst poisoning experiments are crucial in detecting those sub-nanometer M_4 catalysts; and a collaborative paper (3) detailing when, instead, atomically dispersed, single-metal (M_1) catalysts can form, plus how to properly detect their presence in comparison to M_4 or larger, supported-M_n-nanoparticle catalysts. A paper was also published (4) detailing how bimolecular plus autocatalytic agglomeration steps lead to larger nanoparticles being formed from initial, smaller nanoparticles.

Selectivity Control Through Modification of Metal Catalysts with Organic Monolayers

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PROGRAM SCOPE

The overall goal of this work is to investigate the use of organic self-assembled monolayers as modifiers for supported metal catalysts. By tailoring the properties of the monolayer-forming species, one can alter adsorbate-adsorbate interactions to control selectivity in heterogeneous catalysis. A combination of catalyst screening experiments and surface characterization is being used to understand mechanisms by which monolayers can influence catalyst activity and selectivity in several probe reactions.

FY 2012 HIGHLIGHTS

Selectivity promotion by self-assembled monolayers has been demonstrated both in vapor and liquid phase reaction conditions and with Pd and Pt catalysts on a variety of supports. In liquid phase reactions, tuning of monolayer-solvent interactions can play a strong role in modifying selectivity. Modifiers with bulkier ligands (e.g., adamantanethiol) can be used to reduce the sulfur attachment compared to more conventional coatings (e.g., linear alkanethiols). For some vapor phase hydrogenation reactions, this results in a large improvement in catalytic reaction rate. Tuning the properties of the organic function in the modifier has been shown to have a strong effect on selectivity in several hydrogenation reactions, including hydrogenation of cinnamaldehyde, polyunsaturated fatty acids, and nitroaromatic compounds. In some cases, the identity and precise location of a particular organic functional group within the monolayer plays a dominant role in determining catalyst performance, opening the door toward rational catalyst design using organic monolayers.

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

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PROGRAM SCOPE

The goal of the project is to use H• transfer from transition metals to olefins/acetylenes to carry out radical cyclization reactions. Gridnev and Ittel (DuPont) have shown that under H_2, a cobal(II)oxime catalyzes chain transfer during the polymerization of methyl methacrylate, suggesting that a cobalt hydride is present. We are using acceptors like trityl radical (Ar_3C•) to trap these hydrides and to confirm their formation from cobaloximes, and we are trying to determine the strength of their Co–H bonds. We are exploring the usefulness of these Co systems (cobal(II)oximes/H_2) in the catalysis of radical cyclizations. We are using H• transfer to alkynes to generate vinyl radicals, which are more reactive and more synthetically useful than the tertiary alkyl radicals we have generated by H• transfer to alkenes. Because triple bonds add radicals more slowly than analogous double bonds, we predict that there will be a kinetic barrier to the transfer of H• to alkynes. We will continue measuring the rate constants for the transfer of H• from $CpCr(CO)_3H$ (our standard of comparison) to double and triple bonds of all sorts. We are investigating the regeneration of hydrides such as $CpCr(CO)_3H$ from H_2 and the corresponding metalloradicals.

FY 2012 HIGHLIGHTS

Cobal(II)oximes catalyze the addition of H_2 to trityl radicals (or TEMPO). The reaction is second-order in cobalt, first-order in H_2, and zero-order in trityl radicals. The rate-determining step (which is second-order in cobalt and first-order in hydrogen) is the uptake of H_2 by the cobaloxime; the third-order rate constant is 106(3) $M^{-2}\cdot s^{-1}$. Cobal(II)oximes catalyze the radical cyclizations of appropriate dienes under H_2—the H_2 is the only stoichiometric reagent! The reaction of $CpCr(CO)_3H$ with triple bonds occurs by different mechanisms, depending upon the substrate: by H• transfer with phenylacetylene, by electron transfer with dimethyl acetylenedicarboxylate. The cyclization of appropriate alkynes can be catalyzed by $CpCr(CO)_3H$ or a cobal(II)oxime under H_2.

Catalytic Methods to Form Organic Electronic Materials

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Funding: $170,000

PROGRAM SCOPE

This grant has two broad objectives: (1) to synthesize and study hemispheric molecules and (2) to synthesize and study graphitic ribbons. The intellectual thread that ties the two objectives together is the use of strain as a design tool in catalytic systems to create unique 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 2012 HIGHLIGHTS

Through the course of this grant, we have become interested in using strained annulenes and annulynes in the reaction with metal-carbenes and metal-carbynes to perform ring opening alkene and alkyne metathesis polymerization. These polymers will serve as the precursor to electronic materials such as graphene nanoribbons where the width and length is atomically defined. During this funding cycle, we have had three major achievements. (1) We have found that bidentate ligands provide well-controlled ring-opening polymerizations. This work was published in *Macromolecules.* (2) Building off of these results, we have found a new multidentate ligand set that provides a crystalline molybdenum dimer precatalyst that is air and bench stable. The most interesting finding is that this precatalyst can be activated with alcohols and can operate on substrates that have acidic functional groups such as phenols. This work is currently under review for publication. We have filed an invention disclosure on this catalyst system. (3) We have found a means to synthesize a monomer that allows us to create ene-diyne polymers. We are investigating the polymerization of this monomer and the ring closing reaction of its oligomers. Given the expanded substrate scope for our monomers and this new monomer, we feel that these systems will have broad applicability in catalysis in general but more specifically in graphene ribbon synthesis.

Fundamental Studies of Metal Centered Transformations Relevant to Catalysis

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Funding:	$155,000

PROGRAM SCOPE

The specific objectives and research goals of the research performed during the recent grant period have been 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 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 C_1 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 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 CO_2 is crucial for advancing the use of hydrogen as a fuel and for utilizing CO_2 as an effective C_1 source for commodity chemicals.

FY 2012 HIGHLIGHTS

In addition to developing catalytic transformations for the above transformations, it is essential to discover new methods that rely on earth abundant elements. In this regard, we have demonstrated that *tris*(2-pyridylthio)methyl zinc hydride, [Tptm]ZnH, is a multifunctional catalyst that is capable of achieving (1) rapid release of hydrogen by protolytic cleavage of silanes with either water or methanol, and (2) hydrosilylation of aldehydes, ketones and carbon dioxide. For example, [Tptm]ZnH catalyzes the release of three equivalents of H_2 by methanolysis of phenylsilane, with a turnover number of 10^5 and a turnover frequency surpassing 10^6 h^{-1} for the first two equivalents. [Tptm]ZnH also catalyzes the formation of triethoxysilyl formate by hydrosilylation of carbon dioxide with triethoxysilane. Triethoxysilyl formate may be converted into ethyl formate and *N*,*N*-dimethylformamide, thereby providing a means for utilizing carbon dioxide as a C_1 feedstock for the synthesis of useful chemicals.

Benzylzirconium compounds are employed for the synthesis of catalysts for olefin polymerization. Benzyl ligands coordinate to transition metal centers in manifold ways; and the coordination mode is not only expected to influence the intrinsic reactivity of the M–CH_2Ph bond, but could also provide a means to modulate the reactivity of a metal center by stabilizing coordinatively unsaturated centers. In this regard, we have demonstrated that a benzyl ligand attached to zirconium is intrinsically flexible, such that this may contribute to the reactivity of this class of compounds.

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

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Funding: $140,000

PROGRAM SCOPE

The goals of this project are to (1) synthesize well-ordered crystalline mesoporous transition metal oxide (MTMO) materials with monomodal uniform pore sizes; (2) prepare and characterize ordered mesoporous thin films; (3) optimize catalytic activity, selectivity, and stability in oxidation catalysis using amorphous porous oxides and crystalline microporous and mesoporous materials; (4) investigate the role of mesoporous materials in battery systems; and (5) 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, Co_3O_4, 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.

FY 2012 HIGHLIGHTS

We have successfully made uniform monomodal pore sized crystalline walled mesoporous metal oxides that show excellent adsorption and catalytic properties. These materials have been expanded to systems throughout the periodic table that have outstanding thermal stabilities. In the next period, we will focus on the characterization of the mechanism of formation of these materials, which are made of nano-size crystallites that align during synthesis and do not sinter. In addition, we will study specific catalytic activity of these different systems and applications regarding adsorption, sensors, and battery materials.

Understanding the Effects of Surface Chemistry and Microstructure on the Activity and Stability of Pt Electrocatalysts on Non-Carbon Supports

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Funding:	$160,000

PROGRAM SCOPE

The goal of this project is to develop an atomic-level understanding of the effects of the surface chemistry and microstructure of the electrocatalyst support on the activity, stability, and utilization of supported Pt clusters. More specifically, our work aims to uncover the mechanisms by which the support directly manipulates the properties of Pt (i.e., electronic transfer and structure, geometry, etc.) and understand how this impacts activity of Pt towards the oxygen reduction reaction in acid media and Pt cluster stability. This project takes advantage of materials with differing affinity for Pt interaction, including graphitic carbon, functionalized carbons, and electronically conducting ceramic supports. In addition, the crystallinity and structure of the supports are manipulated to understand the influence of microstructure on the electrochemical properties of supported Pt clusters. Using this new fundamental knowledge, our long-term aim is to develop future catalysts with ultra-low platinum loading, high performance, and low degradation rates. Though this work will focus on electrochemical systems, the findings of this study have the potential to impact heterogeneous catalysis in general, where catalyst-support interactions are of great interest.

FY 2012 HIGHLIGHTS

We confirmed two of our fundamental hypothesis, showing that both the activity and stability of Pt can be controlled (improved) using the catalyst support. We observed that this happens through two primary mechanisms: electron donation and preferential faceting, with preferential faceting having a larger effect. This led to a 4-fold increase in the oxygen reduction activity of Pt supported on Tin-doped indium oxide compared with Pt black and Pt/C particles of identical size. We also found that pore sizes in both the micro and meso range (pores < 50 nm) do not impact Pt electrocatalytic activity; however, introduction of controlled surface functional groups can enhance the activity by 2x compared to commercial Pt/C. Finally, both microstructure and surface functionalization can be used to considerably enhance the double-layer capacitance of carbon-based materials, and are promising materials for supercapacitors. In the next period, we plan to mate our experimental results with DFT calculations and further study the preferential particle growth.

Chemical Imaging of Single Metal Nanoparticle Catalysis

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Funding:	$160,000

PROGRAM SCOPE

The long-term goal of this program is to understand the fundamental principles governing the catalytic 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 contains two projects. In the first project, we aim to map out the distributions of active sites on single Au-nanoparticles of various morphologies and probe their spatially resolved catalytic activity and dynamics. In the second project, we aim to understand how the surface structure affects the catalytic activity, mechanism, reactivity inhomogeneity, and temporal catalytic behaviors of Pt-nanoparticles at the single-particle level. These two projects are expected to lead to unprecedented spatial and temporal information on the catalytic properties of nanoparticle catalysts. 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 2012 HIGHLIGHTS

We have successfully developed a single-molecule super-resolution fluorescence microscopy method to spatially resolve catalytic reactions on a single nanocatalyst (Nature Nanotechnology, 2012, 7, 237-241). We discovered complex reactivity patterns on single Au nanorod catalyst. We have also interrogated the catalytic behaviors of single Pt nanoparticles in catalyzing two different reactions, and quantified their activity heterogeneity, dynamics, and structural sensitivity in the respective reactions (Nano Letters, 2012, 12, 1253-1259).

Development and Applications of New Carbonylation Catalysts: Improvements in Regioselectivity, Stereoselectivity, Activity, and Exploration of New Reactions

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Funding:	$160,000

PROGRAM SCOPE

The goal of this research proposal is the development of new catalysts for carbonylation of heterocycles and aldehydes. The project focuses on four main objectives: (1) the development of the next generation of catalysts with enhanced reactivity and selectivity for epoxide carbonylation; (2) the development of new catalysts for regio- and enantioselective carbonylations; (3) the development of catalysts for the carbonylation of more challenging substrates, such as heterocycles with lower ring strain and aldehydes; and (4) the development of routes for the carbonylation of aldehydes and imines for the synthesis of high-value organic building blocks and biodegradable polymer architectures. These objectives are intertwined, and catalyst development and mechanistic insights from one area will be useful for the program as a whole and spur progress in the other areas.

FY 2012 HIGHLIGHTS

We have commenced an expanded exploration of regio- and stereoselective carbonylation of epoxides to develop atom-efficient routes to useful monomers and organic building blocks, and conducted detailed mechanistic studies to understand the factors governing stereo- and regioselectivity. We have discovered an exciting new class of enantioselective epoxide carbonylation catalysts that are capable of the desymmetrization of meso-epoxides, as well as the kinetic resolution of chiral epoxides.

Catalysis of Small Molecule Activation by Proton Coupled Electron Transfer

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Funding:	$160,000

PROGRAM SCOPE

The goal of this project involves the activation of small molecules—O_2 in particular—via coordination to transition metal complexes. We have broadened the scope of the project to utilize new redox-active ligands, and we hope to address N_2-reduction. The overarching goal of this chemistry (hence the title) is the *catalysis of 'proton coupled electron transfer' (PCET – by definition a 'single chemical reaction step involving concerted transfer of both a proton and an electron') to metal bound fragments derived from the most abundant small molecules (i.e., O_2 and N_2)*. Many important chemical problems are tied to this fundamental reaction type. Among these are:

- metal catalyzed oxidations of organic molecules utilizing O_2 as the terminal oxidant (i.e., the original motivation for this project, and one that will continue to be a focus);
- reduction of O_2 to water close to the thermodynamic potential—in other words, the cathode of any fuel cell based on reactions (of H_2, CH_4, CH_3OH, etc.) with O_2;
- fixation of nitrogen at modest temperatures and pressures; and
- transfer of reduced nitrogen species to organic substrates (e.g., aziridination, amination).

Any one of these problems has obvious implications for the generation and utilization of energy on a large scale.

FY 2012 HIGHLIGHTS

We have now completed the synthesis of redox-active tris(pyrazolyl)borate ligands, such as $Tp^{Fc,R}$, where R = H, Me, ^{i}Pr, Fc. Transition metal complexes of these ligands are now being prepared, and the effect of the charge state of the Fc- substituents is being investigated. In parallel developments, we are exploring the chemistry of low-valent, substitutionally labile complexes such as $[Tp^{tBu,Me}M]_2(\mu\text{-}N_2)$, where M = Cr, Mn, Fe. We are searching for hydrogen atom transfer reactions (PCET) that are amenable to detailed kinetic study.

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

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Funding:	$300,000

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 about 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. The purpose of the current renewal proposal is aimed to provide assistance and to develop new sciences/techniques to the catalysis community through the following concerted efforts:

- Dedicated beamtime on two x-ray absorption fine structure (XAFS) beamlines and one additional beamline combining XAFS and x-ray diffraction (XRD)
- Dedicated in-situ reactors for a variety of catalytic and electrocatalytic studies
- A research staff and a postdoctoral fellow to assist the experimental set-up and data analysis
- Training courses and help sessions by the PIs and co-PIs
- Development of new techniques for catalytic and electrocatalytic research
- Coordination of catalysis beamline transfer to the new light source, NSLS II

FY 2012 HIGHLIGHTS

We provided well-maintained, user-friendly, and state-of-the-art synchrotron facilities to over 40 catalysis and electrocatalysis groups in their efforts to perform cutting-edge beamline research. We also offered a successful short course to train students and postdoctoral fellows who are interested in learning synchrotron techniques for catalysis. The SCC also represents a new model for operating synchrotron facilities by providing direct interaction and feedback between funding agencies, beamline scientists, and researchers from academic and national laboratories.

From First Principles Design to Realization of Bimetallic Catalysts for Enhanced Selectivity

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Students:	1 Postdoctoral Fellow(s), 8 Graduate(s), 0 Undergraduate(s)
Funding:	$680,000

PROGRAM SCOPE

The goal of this project is to demonstrate a new paradigm design for improving catalyst selectivity. Our approach is to enhance selectivity by design via the integration of four research components: Theory and modeling; surface science; materials synthesis, characterization, and scale-up; and catalyst and reactor dynamics and optimization. This integrative approach is being applied to catalytic reactions where bimetallic catalysts may be advantageous. The results of our investigations provide the knowledge base for continuing to search for such synergistic bimetallic combinations using fundamental surface science and computational tools while developing synthetic methodologies to fabricate working catalysts based on these discoveries. We are exploring the design and application of bimetallic catalysts to a host of relevant processes for more efficient and cleaner production and utilization of fuels and chemicals.

FY 2012 HIGHLIGHTS

We found that diffusion of H on metal oxide surfaces is enormously accelerated (~16 orders of magnitude at room temperature on iron oxides) by the presence of impurity levels of H_2O vapor in the environment. This finding has wide ranging implications for reactions involving hydrogen and water in the reactants/products mixture.

We have identified the mechanism of decomposition of propylene oxide on the surface of silver catalysts. This work illustrates the complex manifold of sequential reactions that contribute to the difficulty of achieving high selectivity in direct propylene epoxidation with silver catalysts. It identifies reaction channels that need to be closed in effective catalysts for selective propylene epoxidation and helps the further design and improvement of future catalyst. We also performed UHV surface science studies of adsorption geometry and decomposition pathways of propylene oxide on monolayer Ag supported on a Pt surface.

New methods for the synthesis of core-shell nanoparticles have been developed. Pd@Cu core-shell nanoparticles were grown from soluble Cu(II) precursor solutions and on particles of multiple shapes. Seed-mediated growth of Au@Pd core-shell nanocrystals with a variety of controlled sizes and morphologies has also been achieved. These synthesis techniques provide access to structured multimetallic systems that are predicted to have unique catalytic properties in hydrogenation and oxidation reactions.

Novel Photocatalysts with One- and Two-Dimensional Nanostructures

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

PROGRAM SCOPE

Production of solar fuels by photocatalysis is one potential route to reduce the emission of heat-trapping gases into the atmosphere. The most widely applied photocatalyst is TiO_2; but it cannot utilize the solar spectrum efficiently as its band gap is 3.2 eV, and thus it is able to absorb only 3% of sunlight. We have investigated two different avenues towards improving the light absorption capability of semiconductor materials without loss in activity. To this end, the valence band hybridization method of band gap reduction was utilized. This approach introduces new orbitals at the top of the valence band of the semiconductor that can then hybridize with existing orbitals. The hybridization then raises the maximum of the valence band thereby reducing the band gap. This technique has the added advantage of increasing the mobility of oxidizing holes in the now dispersed valence band. In practice, this can be achieved by introducing N 2p or Sn 5s orbitals in the valence band of an oxide.

FY 2012 HIGHLIGHTS

We identified the mechanism by which nitrogen incorporation into the structure of spinel zing gallium oxides reduces the bandgap and increases the photocatalytic degradation rates of model compounds in aqueous environments. The degradation mechanisms were determined to be via the attack by hydroxyl radicals and holes for rhodamine B and cresol, respectively. We also found that addition of Pt as co-catalyst increased the rate of photodegradation, a result attributed to better charge separation.

Structure-Property Relationship in Metal Carbides and Bimetallic Alloys

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Funding: $135,000

PROGRAM SCOPE

It is well known that the electronic and catalytic properties of transition metals can be modified by alloying with carbon to form carbides or with another metal to produce bimetallic alloys. The carbides and bimetallic alloys often demonstrate properties that are distinctively different from those of the pure parent metals. The objective 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. Metal carbides and bimetallic alloys are potential materials to achieve such an objective.

The current research project involves three parallel approaches: (1) fundamental surface science investigations of the reaction mechanisms of several carefully-chosen probe reactions on carbide and bimetallic surfaces, (2) correlation of chemical activities of these surfaces with their electronic properties using a combination of experimental measurements and DFT modeling, (3) synthesis and reactor studies of carbide and bimetallic thin films and supported catalysts to bridge the materials gap and pressure gap between model surface science studies and heterogeneous catalysis and electrocatalysis.

FY 2012 HIGHLIGHTS

Our research efforts in the past year focused primarily on the understanding and control of the activity, selectivity, and stability of bimetallic and carbide materials. Our efforts included three research areas: (1) combining experimental studies and DFT modeling to design bimetallic surfaces for enhanced hydrogenation activity and selectivity, (2) extending general trends on bimetallic single crystal surfaces to polycrystalline films and supported catalysts, and (3) anchoring bimetallic structures on carbide films to enhance both activity and stability. The selection of bimetallic and carbide materials were based on our previous DFT correlation of the chemical properties (hydrogen binding energy) and electronic properties (d-band center) of bimetallic and carbide surfaces.

Principles of Selective 0_2-Based Oxidation by Optimal (Multinuclear) Catalytic Sites

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Funding:	$240,000

PROGRAM SCOPE

Goals of this project are to (1) develop combined experimental and theoretical approaches enabling molecular-level understanding of the mechanisms of selective (non-radical), reductant-free oxidation of organic substrates by O_2 and the oxidation of H_2O catalyzed by metal oxide cluster systems (polyoxometalates or “POMs”) that have two or more proximal and synergistically interacting metal centers; (2) design optimally effective catalysts by careful examination of the experimentally and computationally accessible atomistic parameters of the POM systems, including proximal interacting metal centers, central heteroatom(s), bridging ligands, and counterions; and (3) develop innovative computational methodology enabling understanding of the mechanisms and dynamics of catalytic reactions involving multi-center transition-metal catalysts.

The proposed research addresses the catalytic selective oxidation of organic substrates by O_2 and the catalytic oxidation of H_2O, which is centrally important in most green fuel generation efforts. Realization of synthetic catalysts capable of such transformations remains a monumental challenge. The POM complexes targeted herein, those with two and more adjacent d-electron-containing metals, address core issues of intellectual and potential practical importance and provide a foundation for addressing principles central to realizing optimal synthetic catalysts and understanding related catalytic biological processes.

FY 2012 HIGHLIGHTS

Developing a viable water oxidation catalyst (WOC) has proven particularly challenging. Our ultimate goal is to realize WOCs that have the stability, durability, and accessibility of heterogeneous metal oxide catalysts with the activity, selectivity, and tunability of homogeneous catalysts. To this end, we recently prepared and characterized a molecular, homogeneous catalyst that is by far the fastest WOC to date with rates comparable to that of the OEC in Photosystem II under some conditions. This new WOC, $Na_{10}[Co_4(H_2O)_2(VW_9O_{34})_2]$ (Na_{10}1-V2, sodium salt of the polyanion 1-V2), contains vanadate(V)-centered polyoxometalate ligands and all earth-abundant elements. While 1-V2 and 1-P2—the phosphate-based homogeneous WOC, $[Co_4(OH)_2(PW_9O_{34})_2]^{10-}$ (1-P2) reported earlier—have nearly identical geometrical features, they display distinct electronic structures and, consequently, quite different reactivity and stability; 1-V2 is faster and hydrolytically more stable than its isostructural analogue, 1-P2.

Complementing these efforts is the development of less expensive but reasonably accurate computation methods allowing one to explore more deeply large catalytic systems. To this end, we develop "reactive" force fields that will take into account most of the usual features of standard force fields, while simultaneously addressing bond breaking, bond formation and permutational symmetry of like atoms. During this grant period, we completed fitting and testing a "reactive" force field for Lindqvist POMs, formula: $M_6O_{19}^{n-}$, where M = Nb and Ta. The optimized parameters for the Nb_6 and Ta_6 Lindqvist ions are part of the ReaxFF suite of MD codes and were recently applied to model POM solvation dynamics at various levels of pH.

Alkane Activation and Oxidation on Pd and Pd-Pt Oxide Surfaces

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Funding:	$200,000

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 Pd and Pt oxide surfaces. In our BES project, we are conducting experimental and molecular modeling investigations of the properties and surface chemistry of oxide phases generated on crystalline Pd surfaces in UHV using oxygen atom beams. We are specifically focusing on characterizing the mechanisms that govern the activation and oxidation of alkanes on pure and Pt-modified PdO(101) thin films. By using oxygen atom beams as the oxidant, we have been able to broadly extend the range of oxygen concentrations that can be generated on Pt and Pd surfaces in UHV. This capability has allowed us to characterize the properties of oxide phases that are important in catalytic applications, yet have not been previously explored in detail. A key finding from our project is that alkanes adsorb as strongly-bound σ-complexes on PdO(101) and that the σ-complexes serve as precursors for facile C-H bond activation. Overall, the major goals of our work are to elucidate atomic-level steps involved in alkane oxidation chemistry on Pd oxide surfaces, and develop microscopic models that can ultimately be used to predict reaction rates under practical conditions. The results of this project have a broad impact on the current understanding of technological applications that use Pd and Pt-based catalysts for the oxidation of alkanes and other compounds.

FY 2012 HIGHLIGHTS

We used dispersion-corrected density functional theory (DFT) calculations to investigate the interactions of O_2, CO_2, and small alkanes with the PdO(101) surface, and obtained excellent agreement with our experimental studies of these systems. Of particular significance is our finding that a microkinetic model derived from DFT results quantitatively reproduces the dissociation kinetics and initial bond selectivity of propane on PdO(101). Our comparisons between modeling and experiment reveal that the harmonic oscillator model, which is typically utilized in microkinetic modeling, significantly underestimates the entropies of adsorbed alkanes on PdO(101) and consequently, underestimates propane dissociation rates on PdO(101) by more than two orders of magnitude. Using a microkinetic model that treats two adsorbate motions as unconstrained, we predict propane dissociation rates on PdO(101) that agree to within 20% of experimental values. This result demonstrates the possibility of accurately predicting alkane dissociation kinetics on surfaces and highlights the need for more robust methods to predict adsorbate entropies in microkinetic models.

In Situ NMR/IR/Raman and ab initial DFT Investigations of Pt-Based Mono- and Bi-metallic Nanoscale Electrocatalysts: from Sulfur-Poisoning to Polymer Promoters to Surface Activity Indexes

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Funding:	$170,000

PROGRAM SCOPE

The two primary objectives of the project are to (1) advance significantly our fundamental understanding of sulfur poisoning of Pt-based mono- and bi-metallic nanoscale electrocatalyts through careful interrogation of long- and short-range electronic effects of the poisonous sulfur-metal bonding, and (2) investigate and establish correlations among the surface *d* band center, the frontier orbitals of the metal surface as represented by the surface local density of states at the Fermi level (E_f –LDOS), and the associated electrochemical reactivity. For achieving these objectives, we propose to use surface ^{195}Pt and ^{13}C of chemisorbed ^{13}CO as the key complementary pair of *local* probes of electrode-potential-controlled nuclear magnetic resonance (NMR) spectroscopy to investigate the *local* (surface) electronic alternations of the Pt-based electrocatalysts, in an unprecedented detailed fashion, as functions of sulfur coverage, electrode potential, alloying element (such as Ru/Rh, Sn/Pb, Au/Ag, or other elements), and surface coordination number (particle shape). The ^{195}Pt and ^{13}C NMR have been proven unique in measuring the E_f –LDOS at the probing nuclei. In parallel, the reactivity of the corresponding electrocatalysts towards electro-oxidation of hydrogen and methanol and electro-reduction of oxygen will be characterized in detail by conventional electrochemical methods such as cyclic voltammetry, chronoamperometry, and rotating-disk-based kinetic methods. These investigations will be further complemented by NMR of alloying elements (such as ^{119}Sn, ^{109}Ag, ^{103}Rh, or ^{207}Pb) whenever feasible and by *in situ* surface enhanced infrared and Raman spectroscopy. Additionally, *ab initial* quantum calculations will be employed and intimately integrated with the experimental research to further our fundamental understanding of electrocatalysis in general and S-poisoning in particular. The crosscutting data obtained by the proposed integrated research will be meticulously analyzed by comparing critically to their available counterparts in the gas phase and to available theoretical predictions by which fundamentally important electronic structure–reactivity relationships may be established.

FY 2012 HIGHLIGHTS

(1) Following our major discovery that sulfide anion (S^{2-}) is the species that adsorbs on the Pt surface in FY 2011, we have discovered that the adsorbed sulfide, notwithstanding its conventional reputation as a surface poison, can not only enhance CO and methanol electro-oxidation but also oxygen reduction reaction (ORR).

(2) We have discovered that for heavier polyvinylpyrrolidone (PVP) adsorbed on carbon-supported Pt electrocatalyst, its >C=O can act as a surface bonding on-and-off molecular switch to accommodate more water adsorbed in the methanol oxidation potential region relevant to fuel cell application.

(3) We have discovered that adsorbed iodine can improve substantially the stability of PtCu alloy nanoparticles with strongly enhanced ORR activity.

Developing the Science of Immobilized Molecular Catalysts

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Funding:	$700,000

PROGRAM SCOPE

A team of experimental and computational researchers from multiple universities are collaborating to investigate supported molecular catalysts. Biological catalysts, which operate via (1) cooperative mechanisms, (2) with compartmentalized catalysts, and (3) in cascade process, are the inspiration for our designed catalysts. An emphasis has been placed on understanding the effect of catalyst design/structure on both catalytic productivity and catalyst deactivation, as we hypothesize that limited practical implementation of supported molecular catalysts is mostly related to poor catalyst stability, rather than poor activity or selectivity.

FY 2012 HIGHLIGHTS

Previously, we have shown that cyclo-octene-based cyclic oligomeric supported of Co-salen catalysts are the most active catalysts known for hydrolytic kinetic resolution of epoxides. During the past year, we developed a cross-linked version this catalyst, which facilitates improved catalyst recovery and recycle, making for a more environmentally benign, recyclable catalyst.

In parallel, the team's study of cooperative bimolecular catalysts was extended from the Co-salen system described above to silica-supported, acid-base binfunctional catalysts for aldol coupling reactions. Our studies demonstrated that the aldol reaction, an important reaction in organic synthesis and biofuel production, is most efficient when catalyzed cooperatively by a combination of an amine base coupled with a weak acid or hydrogen bonding partner, like a silanol on a silica surface. This finding was extended to a systematic evaluation of the impact of the spacing between the amine and the partner silanol, showing that an optimal distance can lead to the most efficient catalysis. These findings directly impact the rational design of improved, low cost catalysts for aldol and related reactions.

Early Career: Catalyst Design for Small Molecule Activation of Energy Consequence

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Funding:	$150,000

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., H_2O, N_2, CO_2) 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., N_2, CO_2) 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 2012 HIGHLIGHTS

We have used simple polyamine-based ligands to construct polynuclear reaction sites with the capability to control the local metal ion coordination environment while proximally orienting the metal ions to induce cooperative redox reactivity. This strategy allows numerous permutations permitting a high degree of generality to this approach with many synthetic handles to tune redox and reaction chemistry. Our first published reports showcase the expanded redox flexibility, spin-state tunability, and the capacity to effect multi-electron small molecule activation. The open-shell configuration induced by the weak-field superstructure permits facile functionalization of bound substrates. Future research will primarily focus on incorporating the stoichiometric reactivity into viable catalytic sequences for the breakdown of small molecule substrates.

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

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Funding:	$180,000

PROGRAM SCOPE

As fossil fuel resources become scarcer, there is great incentive for developing more energy-efficient processes. The production of chemicals provides an opportunity for significant reduction in the use of fossil fuel resources. Heterogeneous catalysis is a cornerstone of chemical production; and, thus, improvements in catalytic processes have the potential for meeting these aims. We are investigating fundamental questions about the function of Au alloyed with Ag, Cu and Pd towards the goal of enabling more efficient chemical production. Our work focuses on molecular-level reaction pathways for functionalization of alcohols and polyols—key renewable resources—that are promoted by Au alloyed with Ag, Cu and Pd and applying that knowledge to the development of nanoporous Au alloy catalysts. We are investigating 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, 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 with potential application to the functionalization of feedstocks derived from biomass. 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 test high surface area, nanoporous catalytic materials for these reactions using principles derived from our model studies.

FY 2012 HIGHLIGHTS

Our DOE-sponsored work has focused on oxidative transformations of alcohols induced by metallic Au surfaces. Our primary recent achievements are (1) the development of a mechanistic framework for selective oxidation of alcohols by oxygen adsorbed on metallic Au allowing prediction analogous catalytic reactions; (2) the discovery of a new class of carbonylation reactions, demonstrated for methanol; and (3) demonstration of catalytic oxidation of ethanol using nanoporous Au catalysts under working conditions. An important highlight of our work is the discovery of methanol carbonylation reactions promoted by gold activated by oxygen atoms. This discovery provides an alternative pathway for the production of dimethyl carbonate, which is an essential commodity chemical used in biofuel production and methylation processes. This process occurs at moderate temperatures—just above room temperature—suggesting that low temperature carbonylation promoted by Au is feasible. Our understanding of the mechanism for the carbonylation of methanol is based on fundamental studies that combine x-ray photoelectron and vibrational spectroscopies with reactivity studies. These spectroscopic studies identified the methoxy carbonyl intermediate, which is a versatile synthetic reagent. Thus far, we demonstrated the synthesis of $(CH_3O)_2C{=}O$ (dimethyl carbonate), $(CH_3O)(C_2H_5)O)C{=}O$, $(CH_3O)(C_6H_5)O)C{=}O$, and $(CH_3O)((CH_3)_2N)C{=}O$.

Development of Catalytic Alkylation and Fluoroalkylation Methods

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Funding:	$145,000

PROGRAM SCOPE

Selective alkylation and fluoroalkylation methods will continue to play an important role in synthetic chemistry, and their methods development can impact many areas of basic science. The goal of this program is to use cheap, readily available, and environmentally benign metals to perform synthetic transformations using moieties typically present in natural gas feed stocks and fluorinated materials. It is our goal to understand at the molecular level the details of transformations that could enable the process feasibility for reactions that have thus far remained problematic for palladium. We are focusing on preparing new alkyl and perfluoroalkyl metal complexes to understand the roles of geometry and oxidation states in reductive elimination reactions of these catalytically relevant species. We also aim to develop a new synthetic methodology involving perfluoroalkyl substrates. By employing a mix of focused exploratory chemistry, catalyst screening, and computational chemistry, our goal is to uncover new reactions and to better understand the appropriate ligand platforms in order to manipulate organofluorine compounds for development of efficient catalytic processes using base metals. DOE has had a long-standing interest in the fundamental chemistry of fluorine ever since it was discovered that uranium hexafluoride exhibits a low vapor pressure and could be used to purify isotopically enriched uranium. Fluorination has become popular for other important reasons, like its known ability to increase the oxidative and thermal stability of new materials (e.g., Teflon on a non-stick frying pan and seals that could withstand corrosive conditions) and its role in supporting new energy technologies is expected to grow.

FY 2012 HIGHLIGHTS

We published ten papers resulting from our DOE-funded efforts. We prepared and structurally characterized the first transition metal complex bearing a trifluoromethoxy ligand. We prepared new bis-perfluoroalkyl complexes of nickel and compared the electronic structures to the non-fluorinated counterparts. We developed a new catalytic method to prepare aryl trifluoromethyl sulfides using nickel; an electrocatalytic method to add perfluoroalkyl groups to alkenes; and a new method to oxidatively couple SCF_3 to boronic acids using copper and dioxygen.

Organometallic and Catalytic Chemistry of Functionalized Complexes

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Funding:	$180,000

PROGRAM SCOPE

This project consists of 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 subproject addresses fundamental questions associated with how electron-transfer influences reactions of homogeneous catalysts. We introduce new redox-active ligands of the type $FcCH_2PR_2$ where Fc is a modified ferrocene. These ligands are less non-innocent and more easily installed than traditional non-innocent ligands. The second subproject, 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 subproject 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.

The Reactivity and Structural Dynamics of Supported Metal Nanoclusters Using Electron Microscopy, in situ X-Ray Spectroscopy, Electronic Structure Theories, and Molecular Dynamics Simulations

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Funding:	$640,000

PROGRAM SCOPE

Our collaborative research team will develop and apply integrated (experimental and theoretical) tools to answer questions of structure and mechanism in heterogeneous catalysis. Our program of work will highlight characterizations made of reactions, and adsorbate interactions, involving supported metal nanoclusters. Our goals are to (1) evaluate the cluster bonding states with the support and adsorbates, and understand their transformation as a function of adsorbate pressure and temperature; (2) understand the nature of the interatomic metal-metal bonding and strain patterns for a given thermodynamic state of the cluster; (3) investigate the energetics of environmentally responsive bond strains and their compensation in adsorption energies; (4) characterize and interpret the role of the support in modifying the structural dynamics, bonding energetics, and reactivity of metal clusters;

(5) investigate surface dynamics, compositional states, and reaction barriers; (6) develop a new methodology for in-operando investigations of catalytic reactions using a versatile, portable cell; (7) develop new theoretical methods to study complex interactions occurring between a nanoscale cluster catalyst, its support, and contacting adsorbates; and (8) investigate the mechanisms of exemplary model catalytic reactions to validate a model for characterizing such processes in terms of the fundamental underlying (environmentally responsive) dynamical attributes of atomic bonding and electronic structure.

We highlight the development of general multiplatform methods for characterizing nanoscale catalytic materials under in-operando conditions, using a cell design accommodating in situ high-spatial-resolution, electron-beam structural characterization, high energy resolution x-ray absorption spectroscopy, diffraction, and other complementary spectroscopies. We will employ first-principles theory and computational modeling as independent characterization tools that will bridge existing gaps with experiment—to bridge atomic level understandings in predictive ways to the chemical and rate-centric properties and specific forms of reactivity exhibited in exemplary catalytic reactions carried out over supported nanoscale metal clusters.

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

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Funding:	$150,000

PROGRAM SCOPE

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 reactions at lower temperatures. The current primary focus of this research program is methane oxidation. Steady advances in homogeneous catalysis have led to capabilities for this reaction to run at temperatures as low as 200 °C, which is low enough to make the processing of methane to methanol for broader and simpler distribution economically feasible, but require toxic solutions and complicated handling procedures. We are developing a bi-functional catalyst system, consisting of a metal-organic complex stabilized on a solid surface, which would take advantage of the low temperature capability of a similar homogeneous catalyst complex, but avoid the challenges of a toxic solution medium by instead employing a solid surface support, which can activate molecular oxygen and thus act as an oxygen source for the reaction.

Our work targets key fundamental chemistry problems. *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? What steps are necessary to enable a cooperative chemistry to occur and open opportunities for bi-functional catalyst systems?* Study of these systems will develop the concept of bringing together the advantages of heterogeneous catalysis with those of homogeneous catalysis, and take this a step further by pursuing the objective of a bi-functional system.

FY 2012 HIGHLIGHTS

We have succeeded in surface adsorption and initial analysis of the components for the metal-organic surface catalysts from high-purity sources. In the next period, we will further develop protocols for self-assembly of the catalysts, conduct high-resolution microscopy characterization, and initiate chemical reactivity studies of these new systems.

Synthesis and Exploratory Catalysis of 3D Metals: Group-Transfer, and Alkane Activation and Functionalization with Greenhouse Gases

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Funding:	$155,000

PROGRAM SCOPE

We have embarked on the synthesis and reactivity of low-coordinate, early transition metal fragments (electron rich metal fragments) that can activate and transform greenhouse gases such as dinitrogen, nitrous oxide, and carbon dioxide as well as small molecules (in their elemental form) such as white phosphorus (P_4) into unusual ligand frameworks or commodity reagents. Our ultimate goal is to convert simple but kinetically inert molecules such as N_2 and N_2O into nitride or N_2O based ligands using vanadium complexes, so that we can deliver the N-atom or the O-atom efficiently onto organic molecules (atom-transfer) or alkanes that are often underutilized because they are not good liquid fuels, thereby providing a Green approach to using these gases as oxidants or sources of abundant N and O-atoms. We would like to expand this methodology to titanium and explore rare ligand motifs such as nitride, phosphide and oxides, all of which have the capability of being potent transfer reagents, including the functionalization of C-H bonds in alkanes and arenes (especially the volatile ones). Current efforts are also geared towards synthesizing and elucidating the electronic structure of mononuclear 3d complexes of Fe and Mn, with the ultimate goal of systematically designing true single molecule magnets (SMM) using earth abundant elements.

FY 2012 HIGHLIGHTS

We reported the synthesis and reactivity of the first three-coordinate vanadium(II) complex with small molecules such as N_2O, N_2, S_8, and P_4. Notably, we can isolate fairly stable vanadium dinitrogen complexes as well as low-coordinate vanadium complexes having a terminal nitride ligand or having a reactive *cyclo*-P_3 framework. The reactivity of the later species has been explored, including their redox properties. These systems can be prepared in multigram scales using cheap and easy-to-prepare protocols (as well as ligands). This work was published in the prestigious chemical journal *J. Am. Chem. Soc.* in 2012. In addition, we have completed the spectroscopic and magnetic study of the first mononuclear Fe(III) complex that behaves as a SMM, but that also displays an unusual spin transition from an S = 3/2 to an S = 5/2 state. This complete study was also reported last year in the *J. Am. Chem. Soc.*

Biomimetic Catalysts Responsive to Specific Chemical Signals

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

PROGRAM SCOPE

Conformational control and amphiphilicity are frequently used by nature to control the binding, molecular transport, and catalysis of biomolecules. The overall objective of this project is to employ these principles to develop biomimetic catalysts that can be tuned rationally by specific signals. Supramolecular regulation of the catalyst's microenvironment will modify the activity and selectivity of the catalyst, similar to what happens in sophisticated enzymatic biocatalysts. We have prepared amphiphilic foldamers using an amino-functionalized cholic acid as the monomer. The oligocholates can fold into helices with nanometer-sized internal cavities. Cavities of this size are typically observed only in the tertiary and quaternary structures of proteins but are formed in our foldamers prepared in just a few steps from the monomer. We have demonstrated that the cooperative conformational change of the oligocholates can be exploited to magnify their binding interactions with appropriate guests/substrates, affording extraordinary binding affinities with weak binding forces. Combining simple amphiphilicity principles and efficient click-crosslinking allowed us to prepare water- and oil-soluble core–shell nanoparticles with encapsulated catalysts. These nanoparticles can be readily functionalized at multiple places for further tuning of the catalytic activity.

FY 2012 HIGHLIGHTS

We completed a study to fold the oligocholates in surfactant micelles. The rigidity of the foldamer backbone turned out as the controlling factor in the conformational behavior of the oligocholates in micelles. We also prepared interfacially crosslinked reverse micelles (ICRMs) useful for size-selective phase-transfer catalysis. The ICRMs were used as templates to form subnanometer gold clusters useful for catalysis. When loaded with palladium metals, the Pd@ICRMs were found to catalyze solventless Heck coupling in excellent yields. We also prepared an artificial metalloenzyme by physically trapping a hydrophobic Rh(I)–bisphosphine complex inside the SCM. In comparison to other methods to prepare water-soluble transition metal catalysts, our method required no structural modification of the catalyst. The SCM-entrapment not only enabled hydrophobic alkenes with up to 10 carbons to react in the aqueous biphasic hydrogenation, but also provided the otherwise conventional rhodium catalyst with high selectivity for linear, terminal alkenes and excellent reusability.

Control of Reactivity in Nanoporous Metal/Ionic Liquid Composite Catalysts

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PROGRAM SCOPE

In this program, we examine a new concept in nanostructured heterogeneous catalysis design—ionic liquid (IL)/nanoporous metal (NPM) composites. 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 will be (1) bias of mass transport of reactants to the surface and products away from it and (2) corralling of reactants and products to spatially separate them and reduce side reactions. We will focus particularly 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 already led to significant improvements in aggregate mass activity, and design of new protic ionic liquids in this program will lead to potentially another order of magnitude improvement for this particular reaction. 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 can then be 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 2012 HIGHLIGHTS

A recent innovation from this program is an electrocatalyst comprised of nanoporous nanoparticles encapsulated with an ionic liquid layer only 1 nm thick. These particles show the highest mass activity toward oxygen reduction yet discovered, an effect due to properties of the organic overlayer, which serves to magnify the catalytic activity of the nanoparticles.

Isotopic Studies of O-O Bond Formation during Water Oxidation

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PROGRAM SCOPE

To mimic natural photosynthesis, utilizing light to drive the conversion of water to oxygen and hydrogen, is a major research objective in the basic chemical sciences. Hydrogen gas produced in this way could provide sustainable energy resource that if harvested efficiently, could replace fossil fuels and transform the world as we know it. In order to design photocatalysts that can use sunlight and water to produce solar hydrogen, fundamental chemical mechanisms that allow for catalysis must first be identified. Thus, we have embarked on an examination of oxidaton/reduction reactions mediated by inorganic and organometallic catalysts using natural abundance oxygen isotope fractionation as a probe. This seemingly unique mechanistic approach has actually been used in the earth and atmospheric sciences as a qualitative probe of photosynthetic reactivity in whole cells and cell fractions. Yet, in the absence of defined chemical benchmarks, it has provided little understanding of the underlying chemical mechanisms. Our efforts have concentrated on understanding factors that give rise to oxygen-18 isotope effects on the transition metal-catalyzed oxidation of natural abundance water, examining the O_2 produced using competitive kinetic methods coupled with isotope ratio mass-spectrometry.

FY 2012 HIGHLIGHTS

We have made significant progress in evaluating a number of catalytic and model systems. First-of-a-kind insights have been obtained using a combined experimental and computational approach. Structures of chemical intermediates and specific transition states can now be probed. Specifically, we have developed the ability to measure competitive oxygen-18 kinetic isotope effects (O-18 KIEs) on stoichiometric as well as catalytic reactions. We have also compared the experimental results to the predictions of density functional theory (DFT), which we have calibrated based on related reactions. The calculations provide an indication of energies associated with different chemical pathways and, more importantly, reproduce the changes in bond vibrations that characterize reactivity. Thus, we have demonstrated the ability to both measure and predict natural abundance oxygen-18 isotope effects on the O–O bond formation mechanisms that occur during water oxidation. These results are detailed in two recent articles: (1) “Oxygen Kinetic Isotope Effects upon Catalytic Water Oxidation by a Monomeric Ruthenium Complex.” A. M. Angeles-Boza, J. P. Roth. *Inorg. Chem*. 2012, 51, 4722−4729. (2) “Studies of the Di-Iron(VI) Intermediate in Ferrate-Dependent Oxygen Evolution from Water.” R. Sarma, A. M. Angeles-Boza, D. W. Brinkley, J. P. Roth. *J. Am. Chem. Soc*. 2012, 134, 15371-86. Achieving this objective provides important validation of the ability to evaluate turnover-limiting steps during water oxidation catalysis. The isotopic probes developed, therefore, can be used to illuminate existing and future mechanistic studies.

Nanoscale Molecules under Thermodynamic Control: Digestive Ripening" or "Nanomachining""

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PROGRAM SCOPE

The goal of this project will be to understand the mechanistic details during digestive ripening of thiol capped Au colloids, a process in which a polydisperse sample becomes monodisperse. The scope of digestive ripening for other metals, semiconductors, and insulators will also be carried out. The roles of excess ligand, ligand type, solvent, and temperature in the digestive ripening process are unclear and need to be investigated. Experiments to understand the fate of sulfur bound hydrogen atoms during Au-thiol interactions will also be carried out. In addition to understanding the details of digestive ripening, the catalytic properties of these nanoparticles will be explored. These metal nanoparticles can be incorporated into semiconductor nanoparticles like TiO_2, and the effect of different metal nanoparticle loading toward photocatalytic activity will be studied. The long-term impact of this work will be to develop versatile routes for the gram scale synthesis of monodisperse nanoparticles suitable for catalysis.

FY 2012 HIGHLIGHTS

We have prepared dodecanethiol and phenylethane thiol capped gold nanoparticles by the solvated metal atom dispersion method and by the inverse micelle method. A complete study on size focusing of Au nanoparticles during ligand interactions was done. A thorough study regarding the Au-thiol interactions was performed and found that there is evolution of hydrogen gas when thiols comes into contact with Au nanoparticles, implying that sulphur bound hydrogen atom is not intact during the formation of thiol capped Au nanoparticles. A series of M/TiO_2 nanocomposites were prepared, and the photocatalytic activity towards hydrogen generation from ethanol/water mixtures using these photocatlysts were done. Among the different metals used, Pd was found to be the best with a hydrogen evolution rate of 2.5 mmol/h for 0.25 wt% Pd loading.

Fundamental Surface Structure-Photoactivity Relationships of Semiconductor Mixed Oxides for Splitting of H_2O to H_2/O_2

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Funding: $165,000

PROGRAM SCOPE

The goals of this research program are to (1) determine the bulk and surface anatomy of highly active mixed oxide and oxynitride photocatalysts for splitting of H_2O to H_2 fuel with cutting edge characterization instrumentation (some unique to Lehigh University) and (2) establish fundamental structure-photoactivity relationships for photocatalytic splitting of H_2O that will develop guiding principles for the design of advanced inorganic photocatalysts.

FY 2012 HIGHLIGHTS

The bulk and surface properties of supported $(Rh_{2-y}Cr_yO_3)/(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ mixed oxide and $(Rh/Cr_2O_3)/(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ core/shell visible light activated photocatalysts were investigated with bulk (Raman, UV-vis, and PL) and cutting edge surface (HS-LEIS and HR-XPS) spectroscopic techniques only available at Lehigh University. The bulk molecular and electronic structures of the oxynitride $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ support phase are not affected by the addition of the Rh-Cr NPs. The supported Rh-Cr NPs, however, affected the recombination of excited electrons and holes, revealing their ability to trap electrons and holes and harness them for photocatalytic splitting of water. The supported $Rh_{2-y}Cr_yO_3$ NPs are responsible for evolution of the H_2 (Rh^{+3}) and O_2 (Cr^{+3}) photocatalytic reaction products. The presence of some metallic Rh^o in the supported $(Rh/Cr_2O_3)/(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ core/shell photocatalyst is responsible for its lower water splitting efficiency because the metallic Rh^o catalyzes the undesirable backward reaction of H_2 and O_2 to water. This study establishes, for the first time, the fundamental structure-photoactivity relationships for the novel visible light active supported Rh-Cr/$(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ photocatalysts.

Catalysts for Energy-Efficient Dinitrogen Activation and N-Atom Transfer Processes

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Funding: $200,000

PROGRAM SCOPE

The central hypothesis of the research program is that the unique steric and electronic features of the monocyclopentadienyl (η^5-C_5R_5), monoamidinate $\{\eta^2\text{-}[N(R^1)C(X)N(R^2)]\}$ (CpAm), and guanidinate $\{\eta^2\text{-}[N(R^1)C(X)N(R^2)]\}$ (CpGu) ligand environments are ideally suited for experimentally and computationally investigating groups 4, 5, and 6 early-transition-metal-mediated N_2 activation, N≡N bond cleavage, and N-atom functionalization within several isostructural series of CpAm- and CpGu-based dinuclear $[L_nM]_2(\mu\text{-}N_2)$ complexes in which the nature of the metal center can be varied as a function of group and row position, formal oxidation state, and d^n electron count. Additional goals of the research program include the development of early-transition-metal catalysts that can utilize cheap and inexpensive nitrous oxide, N_2O, and CO_2 as 'green' chemical oxidants for the on-demand production of commodity chemicals, such as (1) the oxidative conversion of isocyanides to isocyanates according to $N_2O + CNR \rightarrow N_2 + OCNR$ and (2) the deoxygenation of CO_2 and oxo transfer to substrates according to $CO_2 + [S] \rightarrow CO + [S]O$.

The specific aims of the project are to pursue a combined experimental and theoretical approach to (1) establish energy profiles for all pathways leading to N_2, N_2O, and CO_2 multiple bond activation and cleavage—including the molecular and electronic structures of ground-state precursors, intermediates, and products as well as those of interconnecting transition states; (2) determine relative energies and barrier heights for all structures and processes as a function of metal group and row position, formal metal oxidation state, and d^n electron count; and (3) elucidate possible roles played by one- and two-electron reduced or oxidized species in facilitating these activation, multiple bond cleavage, and group transfer processes.

FY 2012 HIGHLIGHTS

During the past year, we have reported that the group 6 CpAm M(IV) terminal oxo complexes, $(\eta^5\text{-}C_5Me_5)M(O)[N(iPr)C(Me)N(iPr)$, where Mo and W are catalysts for the $N_2O + CNR \rightarrow N_2 + OCNR$ transformation and the degenerate oxygen atom transfer between CO_2 and CO under near ambient conditions. Further, under an atmosphere of N_2O and CO, the Mo derivative engages in N-N bond cleavage of N_2O through a 'CO-assisted' process. Coordination and cleavage of the N-N triple bond of N_2 has also been accomplished via photolysis of the group 6 dinuclear complexes, $\{(\eta^5\text{-}C_5Me_5)M[N(iPr)\text{-}C(Me)N(iPr)\}_2(\mu\text{-}\eta^1;\eta^1\text{-}N_2)$ (M = Mo, W), and detailed mechanistic studies have confirmed that thermal N-N bond cleavage in the analogous group 5 dinuclear complex, $\{(\eta^5\text{-}C_5Me_5)Ta[N(iPr)C(Me)N(iPr)\}_2(\mu\text{-}\eta^1;\eta^1\text{-}N_2)$, proceeds via an intramolecular end-on to side-on N_2 coordination isomerization.

Catalysts for Energy-Efficient Dinitrogen Activation and N-Atom Transfer Processes

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Sr. Investigator(s):	
Students:	1 Postdoctoral Fellow(s), 3 Graduate(s), 0 Undergraduate(s)
Funding:	\$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

The central hypothesis of the research program is that the unique steric and electronic features of the monocyclopentadienyl $(\eta^5\text{-}C_5R_5)$, monoamidinate $\{\eta^2\text{-}[N(R^1)C(X)N(R^2)]\}$ (CpAm), and guanidinate $\{\eta^2\text{-}[N(R^1)C(X)N(R^2)]\}$ (CpGu) ligand environments are ideally suited for experimentally and computationally investigating groups 4, 5, and 6 early-transition-metal-mediated N_2 activation, N≡N bond cleavage, and N-atom functionalization within several isostructural series of CpAm- and CpGu-based dinuclear $[L_nM]_2(\mu\text{-}N_2)$ complexes in which the nature of the metal center can be varied as a function of group and row position, formal oxidation state, and d^n electron count. Additional goals of the research program include the development of early-transition-metal catalysts that can utilize cheap and inexpensive nitrous oxide, N_2O, and CO_2 as 'green' chemical oxidants for the on-demand production of commodity chemicals, such as (1) the oxidative conversion of isocyanides to isocyanates according to $N_2O + CNR \rightarrow N_2 + OCNR$ and (2) the deoxygenation of CO_2 and oxo transfer to substrates according to $CO_2 + [S] \rightarrow CO + [S]O$.

The specific aims of the project are to pursue a combined experimental and theoretical approach to (1) establish energy profiles for all pathways leading to N_2, N_2O, and CO_2 multiple bond activation and cleavage, including the molecular and electronic structures of ground-state precursors, intermediates, and products as well as those of interconnecting transition states; (2) determine relative energies and barrier heights for all structures and processes as a function of metal group and row position, formal metal oxidation state, and d^n electron count; and (3) elucidate possible roles played by one- and two-electron reduced or oxidized species in facilitating these activation, multiple bond cleavage, and group transfer processes.

FY 2012 HIGHLIGHTS

We have reported that the group 6 CpAm M(IV) terminal oxo complexes, $(\eta^5\text{-}C_5Me_5)M(O)[N(iPr)C(Me)N(iPr)$, where Mo and W are catalysts for the $N_2O + CNR \rightarrow N_2 + OCNR$ transformation and the degenerate oxygen atom transfer between CO_2 and CO under near ambient conditions. Further, under an atmosphere of N_2O and CO, the Mo derivative engages in N-N bond cleavage of N_2O through a 'CO-assisted' process. Coordination and cleavage of the N-N triple bond of N_2 has also been accomplished via photolysis of the group 6 dinuclear complexes, $\{(\eta^5\text{-}C_5Me_5)M[N(iPr)\text{-}C(Me)N(iPr)\}_2(\mu\text{-}\eta^1;\eta^1\text{-}N_2)$ (M = Mo, W), and detailed mechanistic studies have confirmed that thermal N-N bond cleavage in the analogous group 5 dinuclear complex, $\{(\eta^5\text{-}C_5Me_5)Ta[N(iPr)C(Me)N(iPr)\}_2(\mu\text{-}\eta^1;\eta^1\text{-}N_2)$, proceeds via an intramolecular end-on to side-on N_2 coordination isomerization.

Catalysts for the Living Polymerizations of Olefins

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Funding:	$170,000

PROGRAM SCOPE

We have been exploring the use of MonoAlkoxidePyrrolide (MAP) imido alkylidene initiators that contain molybdenum or tungsten for ring-opening metathesis polymerization (ROMP) of selected monomers. MAP species are revolutionizing organic syntheses that involve olefin metathesis, especially since they can be designed to yield only *Z* C=C bonds. We have found that they are also unusual compared to all known metathesis catalysts in that they produce polymers with a high degree of regio and stereochemical regularity, in some cases essentially 100%. These polymers have never been prepared in pure form, and their structures contrast sharply with results obtained with dialkoxide and enantiomerically pure or racemic biphenolate and binaphtholate initiators for fundamental reasons that are continuing to be elucidated. Major features of MAP initiators are that chiral ligands are not present, the metal center itself is a stereogenic center, and mechanistic details can be observed that cannot be observed in the absence of a stereogenic metal center.

FY 2012 HIGHLIGHTS

ROMP polymerization of norbornenes and norbornadienes by MAP species have produced polymers whose regular structures are derived from what we call "stereogenic metal control," a characteristic of which is inversion of configuration at the metal center with each insertion of monomer into the growing polymer chain. The result is formation of cis,syndiotactic polymers. In the case of a racemic monomer, enantiomers are incorporated in an alternating fashion to give "cis,syndiotactic,alt" polymers for the first time. Inversion at the metal is the result of a turnstile exchange of aryloxide and pyrrolide ligands, a rearrangement that is required in order to lose olefin from the metallacyclobutane intermediate in the same manner (trans to the pyrrolide) as the manner in which the monomer added to form the metallacylobutane intermediate. The main finding recently is that another type of rearrangement can take place in certain circumstances. Polymerization of (+)-2,3-dicarbomethoxynorbornene by Mo(NAdamantyl)(CHCMe$_2$Ph)(Pyrrolide)[O-2,6-(2,4,6-i-Pr$_3$)$_2$C$_6$H$_3$] as the initiator forms a >92% trans,isotactic polymer as a consequence of the metallacyclobutane ring in the intermediate "flipping over" at a rate that is fast with respect to aryloxide/pyrrolide exchange; the configuration at the metal does not change as a consequence of this type of rearrangement. This is the first report of the synthesis of a norbornene polymer that has primarily a trans,isotactic structure.

A second project, for which results will be published soon, is the use of MAP species to polymerize 3-substituted cyclooctenes in a cis and head-to-tail fashion, in contrast to the trans polycyclooctenes formed when ruthenium catalysts are employed. Hydrogenation of these polycyclooctenes yields linear polyeethylenes that contain a main chain side group on every eighth carbon atom.

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

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Funding:	$150,000

PROGRAM SCOPE

The objective of this project is to understand the mechanistic aspects behind the cooperative activation of oxygenates by Lewis acid pairs in aqueous media. Specifically, we will investigate how the reactivity of a solid Lewis acid can be modulated by pairing the active site with other Lewis acidic or Lewis basic sites at the molecular level, with the ultimate goal of enhancing activation of targeted functional groups. Although unusual catalytic properties have been attributed to the cooperative effects promoted by such Lewis pairs, virtually no studies exist detailing the use of heterogeneous water-tolerant Lewis pairs. 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 will require closely linking advanced synthesis techniques, detailed kinetic and mechanistic investigations, strict thermodynamic arguments, and comprehensive characterization studies of both materials and reaction intermediates.

FY 2012 HIGHLIGHTS

This project started September 1, 2012. During the first month of the program, a small portfolio of high silica zeolites containing isolated Lewis acid centers was synthesized. Specifically, zeolites with the Beta topology were synthesized in fluoride media and doped with various heteroatoms including tin (Sn), zirconium (Zr), tantalum (Ta), and niobium (Nb). To ensure framework substitution, solids characterization with NMR, IR, and UV-vis is currently underway. In parallel, all catalysts are being benchmarked using test reactions including Bayer Villiger oxidations and MPV reductions. Once benchmarked, catalysts with mixed heteroatoms (e.g., Zr-Al, Sn-Al) that incorporated both Lewis and Bronsted acidity will be produced.

Natural Catalysts for Molten Cellulose Pyrolysis to Targeted Bio-Oils

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Funding:	$160,000

PROGRAM SCOPE

The utilization of lignocellulosic biomass as an alternative reduced-carbon feedstock processed within high-temperature catalytic reactors is limited by a lack of fundamental understanding of the role of catalysts that naturally exist within biomass. The goal of this project is to understand the impact that natural catalysts such as inorganic ions or oxide particles have on high-temperature pyrolysis chemistry within molten cellulose. We have shown that cellulose pyrolysis occurs through a short-lived intermediate liquid through which hundreds of volatile organic compounds are produced. In our experiments, we will elucidate the liquid chemistry and evaluate the impact of natural catalysts on the distribution of volatile products. By constructing a new experimental technique to differentiate the high-temperature homogeneous reaction chemistry from the catalytic chemistry, we will provide the first insight into the role that inorganic catalysts play in creating new pyrolysis reaction pathways. The long-term impact of this work will be to develop fundamental catalytic knowledge that will lead to improved biomass pyrolysis reactors that produce enhanced bio-oils with greater stability and energy content.

FY 2012 HIGHLIGHTS

We have developed a new experimental technique called *Thin-Film Pyrolysis*, which rapidly heats micron-scale films of cellulose to 500°C at 1,000,000 K/min. This technique provides the first high-temperature method for studying the product distributions of pyrolysis chemistries absent mass and heat transfer limitations. Using this technique, we have discovered a strong *chain-length effect*, whereby the product distribution of biopolymer pyrolysis strongly depends on the length of linear biopolymers. Furthermore, we have discovered that α-cyclodextrin serves as a small-molecule surrogate for cellulose. This discovery has led to the first reactive molecular dynamics simulation of reacting cellulose and elucidation of the mechanism of furan formation from cellulose during pyrolysis.

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

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Funding:	$150,000

PROGRAM SCOPE

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 predictive theories that can guide us in a rapid screening and discovery of novel, more efficient multi-component catalysts (e.g., alloys, inter-metallic materials, or promoted catalysts). To accomplish these objectives, we utilize first-principles density functional theory (DFT) calculations, *ab-initio* atomistic thermodynamics and kinetic simulations, as well as a slate of experimental techniques to measure geometric and electronic structure of catalytic materials.

FY 2012 HIGHLIGHTS

Major accomplishments are as follows. (1) 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. (2) This model was utilized to examine the effect of Cs adsorbates on the O_2 dissociation reaction on Ag(111). The studies also focused on the effect of external conditions (partial pressures and temperature) on the promotion mechanism. It was demonstrated that the findings are universal and can be generalized to any system involving electronegative and electropositive adsorbates on metal surfaces. (3) More recently, the framework discussed under (1) was also used to probe the effects of alloying (or the formation of inter-metallic compounds) on the chemical activity of various sites in the alloy. Experimental measurements of the electronic structure of a number of Pt alloys showed that the formation of alloys leads to the changes in the width of electronic bands (specifically the d-band) and that the extent of charge transfer from one element in the alloy to another was very small. These observations allowed us to develop a simple predictive model relating the local geometric structure of alloy sites to their chemical activity. 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. This means that the model can be used to screen very rapidly through a large alloy space seeking optimal alloy catalysts for a particular chemical transformation. We have employed the model to identify optimal Pt alloys for electrochemical oxygen reduction (ORR) reaction as well as a number of Pt-free “costless” alloys. We are currently testing these alloys experimentally.

Bridging Homogeneous and Heterogeneous Catalysis through Ion-Exchangeable Materials

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Funding:	$150,000

PROGRAM SCOPE

The goal of this project is to use ion-exchange reactions to prepare compositionally complex solid-state materials as direct photocatalysts or as visible light-absorbing compounds to use in conjunction with chemical catalysts. The DOE interest in this work is that catalyst structure can be probed under direct working conditions in tethered systems. The three specific aims of this project are to (1) prepare visible-light absorbing oxide phases with high charge-carrier mobility commonly studied for water-oxidation chemistry, (2) undertake the first detailed study comparing directly the electrochemistry and catalytic activity of the dense ceramic powders to the exfoliated 2-D materials, and (3) quantify the effect of surface area and particle size on catalytic turnover in order to tether solution-phase co-catalysts to colloidal nanosheets of these solid-state visible-light absorbers.

FY 2012 HIGHLIGHTS

In this first year of funding, we have established the synthesis methods needed to propel the first aim. We adapted a sol-gel processing technique to prepare TiO_2:(Nb,N)-25 in which 25% of titanium is replaced with niobium, and 2% of oxygen is replaced with nitrogen in the anatase structure. This material shows a significantly smaller band gap: 2.2 eV compared to TiO_2 (3.2 eV). This alloy is catalytically active; it mineralizes methylene blue dye at a rate seven times faster than the TiO_2 control. This work was published in February 2012: *J. Phys. Chem. C* 2012, *116*, 5986. In addition, we have begun work to optimize the band gap by synthesizing a series of co-alloyed compositions in which the percent of niobium varies from 1 – 30% in order to target a completely charge-compensated compound. We find that increased niobium substitution leads to greater solubility of nitrogen. Consequently, faster rates of dye mineralization result. This work was recently submitted for publication.

With regard to small molecules for water oxidation catalysis, we have synthesized the homogeneous phosphonate-modified $[Ru(terpy)(diphos\text{-}bpy)OH_2](PF_6)_2$ water oxidation catalyst. The complex oxidizes water in the dark, and the current focus is etermining optimal adsorption conditions for the catalyst onto anodized TiO_2 electrodes to drive the third aim.

Catalyst Control of Site Selectivity in Catalytic C–H Arylation and Alkylation Reactions

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Funding:	$130,000

PROGRAM SCOPE

The overall goal of this project is to develop transition metal catalysts that can predictably control and modulate the site selectivity of non-directed C–H functionalization reactions. Ultimately, we anticipate that this work will lead to versatile and general catalytic transformations for C–C bond-formation that will greatly facilitate the synthesis of organic compounds, fuels, and chemicals.

A first focus is studying site-selective palladium-catalyzed C–H oxidative coupling reactions. Preliminary examples of these reactions were reported by our group during the previous DOE grant period, and they form valuable C–C bonds from abundant simple arene staring materials in a single step. However, in order to render these transformations useful for applications in the chemical and pharmaceutical industries, it is critical to be able to control site selectivity such that a single product is formed with high selectivity. This section of the project involves conducting a series of experimental and computational studies to understand the factors that control site selectivity in these reactions. These mechanistic insights will then be used to inform new catalyst development.

A second key focus is the development of new transition metal catalysts for controlling site selectivity in C–H arylation reactions. We are specifically targeting high valent platinum and palladium complexes as catalysts, as we hypothesize that these octahedral complexes will enable control of the site selectivity of the C–H activation step. We are also pursuing the use of metal organic frameworks (MOF's) as catalyst supports to control site selectivity and catalyst reactivity as well as limit catalyst decomposition pathways in these reactions.

FY 2012 HIGHLIGHTS

We have conducted detailed computational studies to elucidate the mechanism of palladium catalyzed C–H oxidative coupling reactions. These studies provide important insights into the factors controlling site selectivity in these systems. We have also achieved highly site selective platinum(IV)-catalyzed C–H arylation of a variety of arene substrates and are currently studying the mechanism of this transformation. Finally, we have assembled a series of MOF-supported catalysts and have begun testing their reactivity and selectivity in C–H arylation and other C–H functionalization reactions.

Bio-Inspired Iron Catalysts for Hydrocarbon Oxidations

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Funding:	$165,000

PROGRAM SCOPE

Nonheme iron enzymes catalyze highly stereoselective oxidations of C-H and C=C bonds in the biosphere. Such oxidations can also be of industrial importance. Of particular interest are the Rieske dioxygenases, which catalyze the cis-dihydroxylation of arene double bonds in the biodegradation of aromatic molecules by soil bacteria, and AlkB, which catalyzes the hydroxylation of the terminal methyl group of linear alkanes, typically n-octane, in bacteria that are involved in the cleanup of oil spills. Inspired by these bioinorganic systems, our group has been exploring the use of nonheme iron complexes as catalysts for the oxidation of hydrocarbons using H_2O_2 or O_2 as an environmentally friendly and atom-efficient oxidant. To date, we have identified a family of iron catalysts that carry out alkane hydroxylation and olefin epoxidation and cis-dihydroxylation with high stereoselectivity. The latter reaction represents the first example of iron-catalyzed olefin cis-dihydroxylation and serves as the starting point for developing olefin cis-dihydroxylation catalysts that use earth-abundant and nontoxic iron to replace currently used earth-scarce and toxic osmium catalysts. Besides inventing new iron oxidation catalysts, another important goal is elucidating the mechanisms of action of these novel catalysts, in particular to trap and characterize reactive intermediates involved in the catalysis.

FY 2012 HIGHLIGHTS

First kinetic studies of Fe-catalyzed olefin oxidations with H_2O_2 as oxidant. Until recently, our work on iron-catalyzed oxidations with H_2O_2 as oxidant had been hampered by our inability to carry out kinetic studies. This impediment arises from a requirement to introduce the H_2O_2 oxidant by syringe pumping to minimize the disproportionation of the H_2O_2 oxidant and obtain high conversion of oxidant to product. We have discovered that adding weak acids to the reactions not only increases product yields but also inhibits H_2O_2 disproportionation, thereby enabling us to carry out kinetic studies to be carried out under pseudo-first order conditions. In these studies, we have found that the rate of olefin oxidation is in fact independent of both H_2O_2 and olefin concentrations, leading us to postulate the rate determining step to be the cleavage of the O-O bond of an iron-peroxo intermediate. The kinetic studies can also be extended to *ipso*-hydroxylation of electron-poor benzoic acids, which is also carried out by these catalysts. In all systems studied thus far, the measured rates are within an order of magnitude of each other. Moreover, an H/D solvent kinetic isotope effect of ca. 2 can be observed for olefin epoxidation, olefin cis-dihydroxylation, and ipso-hydroxylation, strongly suggesting a common peroxide activation mechanism where the proton plays a key role. We argue that this step represents the cleavage of the O–O bond to form the high-valent iron-oxo species that carries out substrate oxidation.

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

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Funding:	$150,000

PROGRAM SCOPE

As raw materials for liquid fuels, biomass and natural gas lie at opposite ends of the chemical spectrum. Methane, the primary component of natural gas, is chemically inert and its conversion involves the removal of hydrogen. Conversely, carbohydrates are highly oxygen-functionalized, and the conversion of biomass-to-fuels is limited by oxygen removal and typically involves the addition of hydrogen. We propose to develop kinetic and mechanistic understanding of bifunctional metal-acid catalyst formulations that concurrently process CH_4 and $C_{2\text{-}3}$ oxygenates for the synthesis of hydrocarbon fuels by kinetically coupling biomass-deoxygenation and alkane-dehydrogenation pathways. Our rationale for using CH_4 in deoxygenation reactions is that both CH_4 and H_2 place H atoms within a pool of reactive intermediates, the hydrogen content of which controls the rate and selectivity of O removal reactions. The research methodology combines chemical and structural characterization of the catalyst with transient and steady state kinetic measurements and isotopic tracer methods to probe the identity, reversibility, and kinetic relevance of elementary catalytic steps. Based on a rigorous description of the kinetic and thermodynamic drivers for alkane dehydrogenation in presence and in absence of $C_{2\text{-}3}$ oxygenates over metal and metal carbide catalyst formulations, this research will demonstrate the essential role of the coverage and reactivity of O, H, and C in determining the rate and effectiveness of catalysts in hydrogen-transfer processes relevant for co-processing natural gas and biomass. In the long term, this research will lead to practical and conceptual advancements relevant to the use of simple hydrogen-rich alkanes in biomass deoxygenation reactions.

FY 2012 HIGHLIGHTS

We have developed metal carbide formulations encapsulated in zeolites that are stable for co-processing methane/acetic acid mixtures. Our kinetic and mechanistic studies show that co-processing methane with acetic acid on Mo/ZSM-5 catalysts results in a staged reactor bed with a fraction of the bed upstream being oxidized by acetic acid to form CO/H_2 mixtures in reforming reactions of methane and the remaining fraction downstream accomplishing methane dehydroaromatization reactions. Downstream CH_4 pyrolysis rates can be interpreted in terms of an approach to equilibrium based on the hydrogen formed in the upstream oxidation zone to rigorously show that forward rates for CH_4 dehydroaromatization are unchanged in presence of acetic acid.

Polynuclear Aromatic Hydrocarbons with Curved Surfaces: Buckybowls

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Funding: $135,000

PROGRAM SCOPE

This program deals with the synthesis, structural study, and chemistry of curved-surface, polynuclear aromatic hydrocarbons (PAHs) with carbon frameworks that can be identified on the buckminsterfullerene C_{60} surface, known as *buckybowls* or *fullerene fragments*. Previous work under this DOE-sponsored program resulted in development of practical methodology for the gram-scale solution synthesis of corannulene and some of its derivatives. Now we can use the smaller buckybowls as starting materials for the solution synthesis of larger systems. The most useful synthons developed in our laboratory are isocorannulenofuran (a diene) and 2-trimethylsilylcorannulenyl trifluoromethanesulfonate (a precursor for 1,2-didehydrocorannulene, a reactive dienophile). Our synthetic methodology can be used to prepare large curved-surface molecular networks with novel properties. Significant effort is devoted to the synthesis of “molecular clips” with corannulene pincers (e.g., buckycatcher) that can act as molecular receptors for various guest molecules including fullerenes, which bind through the $\pi - \pi$ convex-concave stacking of the curved conjugated carbon networks (C_{60}@buckycatcher).

FY 2012 HIGHLIGHTS

We have prepared a potential molecular clip with three corannulene pincers located on cyclotriveratrylene scaffold. However, ^{1}H NMR titration experiment provided its association constants of K_{as} = 1500 and 1200 M^{-1} with C_{60} and C_{70}, respectively, significantly lower than the analogous association constants of buckycatcher (8600 and 6800 M^{-1}, respectively). While the binding energies of the tridental molecular clip with both fullerenes are expected to be higher than in the case of buckycatcher, the lower association constants of the previous clip underline the importance of the entropy and solvation penalties associated with the formation of such supramolecular assemblies.

The collaborative study with Wolfgang Heinert and Jiangfeng Du and co-workers showed that the columnar ordering of C_{60} cages in the inclusion complexes of fullerenes with buckycatcher can be used for the zero-field splitting modifications of the endohedral N@C_{60} radical. EPR studies provided the accessible zero-field splitting of N@C_{60}@buckycatcher with the *D* value of ~14.80 MHz, which is the largest from the similar complexes formed by non-covalent interaction between N@C_{60} and various molecular holders. It is therefore concluded that the electronic structure and the relaxation properties of N@C_{60}@buckycatcher complex makes it a possible qubit for quantum-information processing (QIP).

Late Transition Metal M-OR Chemistry and d^6 Metal Complex Photoeliminations

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Funding: $130,000

PROGRAM SCOPE

Through this program, we aim to understand and control photoelimination reactions from d^6 transition metal complexes as part of a solar energy storage cycle. Specific objectives include: (1) delineating the molecular bromine photoelimination mechanism(s) for Pt(IV) complexes, (2) extending the molecular bromine elimination chemistry to molecular chlorine and to hydrogen peroxide (an alternative water splitting process), and (3) extending the Pt(IV) chemistry to Ir(III) complexes.

FY 2012 HIGHLIGHTS

In collaboration with Dr. Hoff (Miami), we (1) obtained benchmark calorimetric data for the oxidative addition of molecular bromine to Pt(II) complexes, (2) identified the M06 functional as the best DFT functional for matching the calorimetric data, (3) achieved record quantum yields (50-80%) for bromine photoelimination from a transition metal dibromo complex, and (4) shifted the Pt(IV) complex strong π-π absorption bands from the uv into the visible by extending the aromatic chromophore to perylene groups.

In collaboration with Dr. Rack (Ohio), we (1) obtained femtosecond transients for the excitation of several Pt(IV) bromo complexes, (2) used DFT to identify a potential pathway for bromine photoelimination from Pt(IV) bromo complexes, and (3) began our expansion into the chloro and hydroxo Pt(IV) complexes and Ir(III) analogs.

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

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Funding: $170,000

PROGRAM SCOPE

Our overall research goals are to explore new aspects of the relationship between nanoscale features and heterogeneous chemistry as well as electrochemistry. We focus on atomically rough morphologically unstable surfaces of catalytic metals that can undergo nanoscale faceting upon annealing in gas or covered by monolayer metal or gas followed by annealing in vacuum. We will mainly investigate the structure of faceted surfaces, reactivity of faceted surfaces in heterogeneous reactions and electrochemical reactions which are related to air pollution control and hydrogen generation, and the use of faceted surfaces as nanotemplates for growth of metallic nanoclusters and synthesis of nanoscale model electrocatalysts. We have discovered that certain metals such as ruthenium and rhenium with high index planes can undergo nano-faceting upon annealing in some gases. Our studies show that it is possible to tailor the metal surface morphology by choosing the appropriate adsorbate, adsorbate coverage, and annealing conditions. Significantly, using carbon-covered faceted Re surface as a nanotemplate, we have successfully fabricated a nanostructured model electrocatalyst, illustrating the potential for future studies of nanostructured bimetallic systems relevant to electrocatalytic reactions. We have found that the oxygen-covered ruthenium surface facilitates the growth of gold nanoclusters at room temperature. Those nanoparticles preferentially nucleate and grow within valleys of the facets. Notably, we have developed a routine procedure to prepare clean faceted iridium surfaces by removing oxygen from oxygen-covered faceted iridium surfaces via reaction with hydrogen at low temperature. The generation of clean planar iridium surface and clean faceted iridium surface enables exploration of structure sensitivity and size effects in surface chemistry over unsupported iridium, which excludes not only the influence of a support material but also effects that result from changes in catalyst morphology induced by the variation in particle size common to supported catalysts.

FY 2012 HIGHLIGHTS

We have performed detailed characterization of C-induced faceting of Re(11-21) using a combined experimental and theoretical approach. We have synthesized monolayer Pt electrocatalysts supported on faceted C/Re(11-21). We have tailored the morphology of oxygen-covered faceted Ru(11-21) by changing annealing temperature. We discovered a very high activity of planar and faceted Ir(210) for oxidation of CO by NO and reduction of NO by acetylene with high selectivity to N_2. We found size effects in oxidation of CO by NO on faceted Ir(210) for average facet sizes of 5-14 nm but no evidence for size effects in reduction of NO by acetylene on the same Ir. We performed DFT and TPD study of adsorption and desorption on planar and faceted Ir(210).

Mechanisms of N-H Bond Formation Relevant to Nitrogen Fixation

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Funding:	$120,000

PROGRAM SCOPE

The focus of this program is the nitrogen atom transfer reactivity of isolable iron nitride complexes under investigation. Tripodal ligands that enforce three-fold symmetry are known to stabilize these ligands. However, the nitrogen atom transfer reactivity of these complexes tends to be modest; and, therefore, new strategies are required to increase their reactivity.

Insights derived from electronic structure considerations are being used as principles for the design of more reactive iron nitride complexes. To achieve this goal, the project aims to synthesize iron nitride complexes (in multiple oxidation states) supported by new tris(carbene)borate ligands that differ in their donor strength. The influence of the tripodal supporting ligand on the scope of two-electron nitrogen atom transfer reactions, particularly towards unsaturated hydrocarbons, will be investigated. A longer term goal is the development of nitrogen atom transfer cycles for the atom-economical synthesis of nitrogen-containing heterocycles.

FY 2012 HIGHLIGHTS

Cycloalkenes and styrenes react with the iron(IV) nitride complexes to form coordinated aziridino ligands, while 1,3-dienes undergo cycloaddition reactions to yield 2,5-dihydropyrrolo ligands. When 1,3-cyclohexadiene is used as a substrate, the resulting 2,5-dihydropyrrolo ligand undergoes a retro-Diels-Alder reaction to provide a κ^5-pyrrole complex. Full characterization of the products and mechanistic investigations are in progress. Spectroscopic characterization (ENDOR) and preliminary investigations into the reactivity of an iron(V) nitride have been undertaken.

New tris(carbene)borate ligands using benzimidazol-2-ylidene and 1,3,4-triazolyl-2-ylidene donors have been prepared and their donor strength evaluated in $\{NiNO\}^{10}$ complexes. These ligands are expected to increase the reactivity of the corresponding iron(IV) nitride complexes. Surprisingly, a tris(carbene)borate ligand based on mesoionic *N*-heterocylic donors is less strongly donating than anticipated from the trends observed with monodentate *N*-heterocyclic donors. A computational approach for directing the synthesis of new tris(carbene)borate donors has therefore been developed. This strategy has directed us towards the synthesis of ligands based on imidazol-4-ylidene donors, whose synthesis is currently in progress.

Direct Partial Oxidations Using Molecular Oxygen

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Funding:	$250,000

PROGRAM SCOPE

The goal of this collaborative effort between the Kemp group at the University of New Mexico and the Goldberg group at the University of Washington, Seattle, is to develop selective partial oxidation catalysts that utilize molecular oxygen directly rather than using less environmentally-friendly and activated forms of oxygen, such as peroxides. To attack this problem, we have proposed a catalytic cycle that begins with the insertion of gaseous oxygen into a metal-hydride bond to form a metal hydroperoxide. Next, selective transfer of an O-atom from this hydroperoxide to a substrate is proposed to form the oxidized substrate, leaving the metal hydroxide as the by-product. Reaction of the metal hydroxide with hydrogen eliminates water and regenerates the initial metal hydride complex, thus completing the catalytic cycle. As a major part of our efforts, we are studying each of the proposed individual steps in isolation in order to understand more fundamentally how each of these reactions occur. Insertion of oxygen into metal-hydride bonds, transfer of O atoms, and reaction of hydrogen with metal hydroxides are all fundamental reactions that occur in other catalytic projects. While the majority of our work involves preparing homogeneous catalysts, in a step-out study, we are also investigating heterogeneous Cu-based catalysts to effect this transformation. Density functional theory studies have greatly aided our success on this project. Our long-term goal in this project is to develop selective oxidation catalysts, in particular epoxidation catalysts, which utilize oxygen gas directly for a wide variety of organic and inorganic substrates.

FY 2012 HIGHLIGHTS

We have prepared and characterized a number of pincer-ligated metal complexes proposed to be active components in the catalytic cycle. In this effort, we also developed preparations for asymmetric PNP-ligands, a new family of ligands that should prove useful for many in the community. We also completed mechanistic studies of the hydrogenolysis of Pd-OH and Pd-OR complexes, including understanding the effects when hemilabile pincer ligands were used both experimentally and theoretically. In computational studies, we investigated the effects of the electron donating ability of various substrates on the O-atom transfer reaction, and also determined the effects of the *cis*-ligands in pincer-ligated Pd-H complexes upon the insertion of oxygen.

Nanostructured Catalysts for Hydrogen Generation from Renewable Feedstocks

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Funding:	$225,000

PROGRAM SCOPE

The objective of the proposed research is to gain fundamental understanding of complex, multi-component catalysts through an investigation of catalytic processes occurring on system sub-components (the metal phase and the support) and synergistic interactions among the catalyst system components. To facilitate the mechanistic and reaction studies, we are developing methods for the synthesis of catalysts that are well-defined: single phase, uniform composition metallic alloy powders. We are also synthesizing oxides of controlled morphology that expose well-defined single facets so that the role of the oxide phase can be studied. These catalysts are being studied using novel analytical approaches including the use of in-situ microscopy and spectroscopy techniques. The research program is comprehensive in nature and includes detailed kinetic measurements with high surface area catalysts, synthesis of novel catalytic materials with controlled metal deposition and morphology, mechanistic studies using single crystals, detailed catalyst characterization, and state-of-the-art density functional theory (DFT) computations of catalyst structure and reactivity.

FY 2012 HIGHLIGHTS

We have performed operando EXAFS studies of isolated single atom Pd sites for CO oxidation. We have developed a novel approach for the synthesis of catalysts from liquid phase precursors using room temperature reduction without any ligands or surfactants. This method allows us to deposit metal nanoparticles on any support, with controlled size and without any limitations imposed by speciation of precursors in aqueous solutions, and the point of zero charge which limits which precursor can be used on a specific support. By using a combination of in-situ XRD and EXAFS, we studied the phase transformation of PdZn mixed oxides into the ordered intermetallic phases. We have developed methods to synthesize phase pure cubic, orthorhombic and tetragonal phases of PdZn. These materials will next be tested for steam reforming of methanol and ethanol. We have also investigated the reaction pathways of steam reforming of oxygenates on Co surfaces using an integrated experimental and theory approach. On small Co nanoparticles (several nanometers in diameter), it was found that dehydrogenation of oxygenates, followed by C-C cleavage and oxidation of C1 species can be facilitated to minimize the formation of coke and methane, which is due to the facile water dissociation on small Co nanoparticles. We have further confirmed that Zn addition to Co on CeO_2 support further enhances the oxidation of $–CH_3$ in ethanol molecule during steam reforming, likely due to the modification of Co electronic properties by Zn. We will further correlate the surface chemistry with Co surface properties in both vapor and aqueous phase to provide insight in controlling chemical transformations in biomass conversion.

Novel Transport of Porous and Composite Nanostructures

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Funding:	$180,000

A summary for this program was not available at press time.

Oxidative Addition at Anomeric Centers in the Pursuit of Value-Added Fine Chemical Feedstocks From Cardboard and Potatoes

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Funding:	$145,000

PROGRAM SCOPE

We wish to discover catalysts and approaches that will enable the conversion of polysaccharides (e.g., cellulose, starch) into C_6 feedstocks for synthesizing highly functionalized value-added materials for the fine chemical industry. Converting cellulosic biomass into fuels is additionally important, and we envision our efforts may impact this effort as well.

FY 2012 HIGHLIGHTS

To convert glycosyl halides to *C*-glycosides under mild conditions, we have developed a system in which a glycosyl radical is generated via a photocatalyst, essentially harnessing visible light to effect a chemical transformation. The glycosyl radical is then trapped by an electron-deficient alkene, forming the desired *C*-glycoside. Efficient on small scales but plagued by low yields on larger scales, the reaction was found to absorb the vast majority of available light within a short distance of the vessel wall. To overcome this limitation, we built a continuous photoflow reactor to irradiate the reaction mixture while it flowed through a thin transparent tube, rendering multi-gram reactions equally as efficient as milligram-scale reactions. We then refined a method for monitoring the progress of a reaction in the photoflow reactor, which allowed us to optimize the reaction conditions for a variety of carbohydrate and alkene substrates and widen the scope of our photomediated *C*-glycoside synthesis.

Toward the defunctionalization of sugars for fuel applications, we have examined the use of iridium pincer catalysts for the hydrosilylative reduction of sugars. Thus far, we have developed a system for the complete reduction of silyl-protected glucose to a mixture of hexane isomers. The reduction pathway and hexane isomer distribution was sensitive to the protecting group of the anomeric (C_1) alcohol. In the reduction of fully silylated glucose, the dominant pathway was initiated by a ring opening process, which was followed by complete reduction to alkanes with n-hexane as the major product. In contrast, using a methyl-protecting group at C_1 led to selective C_1 reduction, initiating an alternative reaction pathway that yielded the hexane isomers 2- and 3-methylpentane as the major products. The reaction rate was affected by the silane, with the less hindered Et_2SiH_2 giving the fastest rates. Studies on the role of sugar, catalyst, and silane on the efficiency and hexane selectivity of this reaction will continue into the next period.

Modeling of Late Transition Metal Catalysts for Energy Applications

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Funding:	$100,000

PROGRAM SCOPE

Grant DE-FG02-03ER15387 involves two major research thrusts: (1) modeling C—H bond functionalization via catalytic hydroarylation and (2) catalytic reactions of Earth-abundant *3d* transition metals. The latter requires modeling of highly coordinatively unsaturated complexes and is motivated by their critical importance in homogeneous and heterogeneous catalysis. Additionally, such materials are typically not amenable to direct experimental interrogation, and thus our modeling can make (and has made) important contributions to understanding their catalytic chemistry.

Hydroarylation is important for single-step alkylarene synthesis from hydrocarbons and olefins. Alkylarenes are produced on an enormous scale, via Friedel-Crafts chemistry, which requires chlorinated intermediates and thus two reaction steps from hydrocarbon starting materials. With fellow DOE-BES grantee Prof. Brent Gunnoe (UVa), we have developed a fundamental understanding of how different steps in the hydroarylation cycle (plus side reactions) respond to changes in the stereoelectronic profile of the metal and ligands in order to rationally develop more active and selective catalysts.

FY 2012 HIGHLIGHTS

Nine refereed publications acknowledging DOE-BES support via DE-FG02-03ER15387 were published in the past year. Our DOE-BES research was widely disseminated via numerous invited seminars by the PI and junior and faculty research collaborators. DE-FG02-03ER15387 supported the research of eight early career scientists (six Ph.D. students; two postdoctorals) at UNT.

Two papers appeared in the past year discussing our initial research in hydroarylation catalysis by non-octahedral complexes. Research highlights of the past year include delineation of the mechanism of olefin hydroarylation by square planar Pt^{II} complexes. DFT modeling also probed the exciting observation of styrene as a by-product (which we are studying with our experimental collaborators to enhance). Extension of the modeling studies to more Earth-abundant nickel congeners was performed, and these complexes emerged as worthy subjects for further research, experimentally and computationally. Finally, study of Ni and Pt hydroarylation catalysts indicates fundamental difficulties in using structure-property relationships in design vis-à-vis “reverse engineering” base metal replacements from current precious metal catalysts.

Within the second research thrust, we focused on two novel two-coordinate complexes: the first two-coordinate imido complex (of nickel) and a “masked” two coordinate complex (of cobalt). Additionally, in collaboration with the Warren Group (Georgetown), we delineated a novel hydrogen atom abstraction (HAA)/radical rebound pathway for nickel-catalyzed amination of hydrocarbons, which also supported our proposed mechanisms from our group’s earlier DFT studies of C—H activation by Ni-oxo and -imido complexes. The more recent research yielded a novel twist in that after initial HAA of the substrate (RH), there was a competition between radical collapse on to another equivalent of Ni-imide $\{[Ni]{=}NR' + R^{\bullet} \rightarrow [Ni]\text{-}NRR'\}$ versus Ni-amide $\{[Ni]\text{-}NHR' + R^{\bullet} \rightarrow [Ni]\text{—}NHRR'\}$ (the latter yields the desired amine product).

Institute for Catalysis in Energy Processes

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Funding: $1,000,000

PROGRAM SCOPE

The Institute for Catalysis in Energy Processes (ICEP) is a joint venture of the Northwestern University Center for Catalysis and Surface Science and Argonne National Laboratory. It is organized into three highly integrated efforts. Two of these comprise the scientific themes: (1) Chemical Catalysis – Selective Oxidation of Light Alkanes to Fuels and (2) Photocatalysis – Reduction of Carbon Oxides. Research activities of ICEP are in synthesis of catalytic materials, in measurements that reveal catalyst properties and chemistry, and in theory and modeling to understand properties, measurements, and chemistry. In many cases, ICEP researchers are the inventors or developers of the methods that can be brought to bear on catalytic systems. The third effort is a natural outgrowth of these strengths. It provides the research expertise for advancing the scientific themes through the application and development of both experimental methods and theory.

Understanding the elementary catalytic steps in selective oxidation of light alkanes to oxygenates, with an ultimate goal to achieve the ability to design and manipulate selective catalytic sites, is the major objective of the Chemical Catalysis theme. Understanding the elementary steps in the photocatalytic reduction of CO_2 on oxide surfaces is the major objective of the Photocatalysis theme. An important aspect of the ongoing ICEP research is the continued advancement and development of both synthesis and characterization methods which is carried out in the Research Expertise theme.

FY 2012 HIGHLIGHTS

The major activity in Chemical Catalysis has been in the preparation of novel catalytic materials by hydrothermal synthesis, atomic layer deposition, and organometallic grafting. The materials encompass perovskite nanocrystal supports, supported metal nanoparticles, supported oxide species, and metal-organic frameworks. The characterization of these materials has led to exceptionally active Pt catalysts for alkane oxidation, single-site catalysts that are highly selective for oxidation, the discovery of new catalytic vanadium oxide species, and the development of a bond-valance-sums approach to understand oxide surface structure.

Photocatalysis research focused on elucidating the mechanism of CO_2 reduction and the development of higher activity photocatalysts based on titania. In the mechanistic studies, H-atoms, methoxy, and methyl radical intermediates were detected by EPR in the reduction of CO_2 photocatalyzed by titania. Computational studies predicted two possible reaction pathways for reduction of CO_2 to formic acid with the first steps being a concerted 2 electron one proton transfer to CO_2 or a one-electron transfer to CO_2 to form Ti^{4+}-OCO•--Ti^{4+} as an intermediate.

Molecular Nanocages for Catalysis: An Investigation of Effect of Active Site Environment

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Funding:	$170,000

PROGRAM SCOPE

High product selectivity in catalytic chemical processes reduces the energy demand for downstream purification. Since enzymes have evolved to become highly selective and active, it is the objective of this project to incorporate enzyme functionalities into artificial catalytic structures so as to capture the desirable features of enzymes with materials that are more stable and tolerant to process conditions, such as temperature, concentration, and pH. One essential property of the active center of an enzyme is the ability to exert cooperative effect, in which two or more functional groups act synergistically to influence the energetics and/or transformation pathway of a chemical reaction. We plan to acquire knowledge, develop insight, and incorporate cooperativity into nonbiological structures, in a confined space of molecular dimension that is similar to the protein pocket of an enzyme. Our strategy is to

(1) develop know-how in synthetic techniques in order to synthesize the desired structures and (2) demonstrate cooperativity in a catalytic reaction based on the designed structure.

We have demonstrated the versatility of siloxane chemistry in the construction of catalytic structure of interest. This includes the formation of nanocages with interior functional groups, and symmetric and asymmetric oligomeric ligands with functional groups at desired positions. These structures have demonstrated unusual properties, such as unprecedented high pKs shifts of interior amino groups in a nanocage, and ability to stabilize soluble Pd catalysts against precipitation in selective oxidation catalysis.

FY 2012 HIGHLIGHTS

We have made significant progress in developing a synthetic method that permits introduction of multiple functionality with precise positioning. The method involves a designed molecule with a cleavable, silyl ester bond at a prescribed position and functional groups at the terminal positions that can be used to anchor the molecule on a support surface. Very importantly, the nature of the cleavable bond is such that after cleavage, one of the newly created terminals is a silanol, which can react easily to form other targeted functionality. This is a major step towards custom-design of catalytic structures for high selectivity in targeted reactions.

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

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Funding:	$185,000

PROGRAM SCOPE

The scope of this program is to explore, model, understand, elaborate, and exploit pathways by which organometallic molecules of varying nuclearity undergo chemisorption, activation, and catalytic activity enhancement on selected solid surfaces. Such processes closely connect to real-world, large-scale industrial hydrocarbon processes and the goal of manufacturing cleaner, greener, more environmentally acceptable products, including those from renewal resources. Research combines precatalyst synthesis, chemisorptive surface chemistry, homogeneous analogue catalysis, x-ray diffraction structural analysis, and computation/modeling, and involves collaboration with national laboratory and industry researchers. Specific objectives in the past year were (1) characterize mononuclear and binuclear organometallic molecule chemisorption on “super Brønsted acid” oxides where 100% of the sites are catalytically signficant, (2) synthesize and characterize mononuclear and polynuclear catalyst precursors for both surface and homogeneous catalysis, (3) use this information to produce new types of efficient energy storage materials via in-situ catalytic polymerization, and (4) computationally model both chemisorbed catalysts and their reactivity modes.

FY 2012 HIGHLIGHTS

(1) Surface Structural-Chemical Characterization of a Single-Site d^0 Heterogeneous Arene Hydrogenation Catalyst Having 100% Active Sites. The structural characterization of the catalytically significant sites on solid catalysts is frequently tenuous since their fraction, among all sites, is generally low. Here we report the combined application of Zr x-ray absorption fine structure (XAFS) spectroscopy, solid state ^{13}C-CPMS-NMR spectroscopy, and periodic density functional theory (DFT) to characterize the adsorption products and chemistry of the precatalysts $(\eta^5\text{-}C_5H_5)_2ZrR_2$ (R = H, CH_3) and $[\eta^5\text{-}C_5(CH_3)_5]Zr(CH_3)_3$ adsorbed on Brønsted super-acidic sulfated alumina (AlS). The latter surface complex is exceptionally active for benzene hydrogenation with ~100% of the Zr sites catalytically significant as determined by kinetic poisoning experiments. The XAFS, ^{13}C-CPMS-NMR, and DFT data indicate formation of organozirconium cations having a largely electrostatic $[\eta^5\text{-}C_5(CH_3)_5]Zr(CH_3)_2^+\cdots AlS^-$ interaction with greatly elongated $Zr\cdots O_{AlS}$ distances of ~2.35(2) Å. The catalytic benzene hydrogenation cycle is stepwise understandable by DFT, and proceeds via turnover-limiting H_2 delivery to surface $[\eta^5\text{-}C_5(CH_3)_5]ZrH_2(\text{benzene})^+\cdots AlS^-$ species, observable by both the solid state NMR and XAFS techniques.

(2) Surface Catalytic Synthesis of Energy Storage Materials. Materials combining the processability and mechanical properties of inexpensive polymers with the high dielectric constants of oxide nanoparticles are desirable for energy storage applications as in large-scale capacitors. In this work, a series of metal oxide-polyolefin nanocomposites were synthesized via in-situ catalytic olefin polymerization using the single-site organo-group 4 catalysts immobilized on methylaluminoxane-treated $BaTiO_3$, ZrO_2, 8 mol% yttria-stabilized zirconia, *sphere*-shaped TiO_2 nanoparticles, and metallic aluminum nanoparticles. The resulting composites were characterized by x-ray diffraction, SEM, TEM, ^{13}C NMR, DSC, and dielectric measurements. TEM shows that the nanoparticles are well-dispersed in the polymer matrix. Electrical measurements reveal that the oxide nanocomposites have leakage current densities as low as ~ 10^{-6}-10^{-8} A/cm^2 and permittivities as high as 6.1. The energy storage densities of these nanocomposites are as high as 9.4 J/cm^3. In the case of the metallic nanocomposites, permittivties as high as 6.5 are maintained up to frequencies as high as 7 GHz.

Templating Routes to Supported Oxide Catalysts by Design

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Funding:	$155,000

PROGRAM SCOPE

The goal of this project is to develop design and synthesis methods for supported oxide catalysts. Atom-precise syntheses of solid catalysts are a long-standing goal in catalysis science, which promise improved catalyst selectivity and activity. Control over support oxide structures is to be achieved through three routes that template a particular metal oxide structure. Metal precursors with coordinating ligands, with or without structure-promoting alkali cations, are used to synthesize highly dispersed metal oxides for use in selective oxidation applications. Pre-formed metal oxide clusters of different nuclearity (monomeric, dimeric, tetrameric, etc.) are being explored as precursors for standard exchange and incipient wetness techniques in order to decouple metal oxide loading and extent of aggregation.

Finally, liquid or vapor atomic layer deposition are carried out over oxide supports or catalysts that have been modified with single molecule organic templates. After template removal, surface nanocavities are generated in the new, supported oxide film. These nanocavities are proposed for subsequent use as inorganic templates for other metal oxide clusters or for stabilizing isolated metal cations. Alternately, the nanocavities themselves are proposed to lead to shape-selective reactivity through a sieving phenomenon, and control over the accessibility and structure of oxide-oxide interfaces.

FY 2012 HIGHLIGHTS

This grant year saw the acceptance of two key manuscripts citing this grant for support. In the first, recently published in *Journal of Catalysis*, we showed that the structure of FeOx on SiO_2 could be controlled carefully through the use of chelating Fe ethylenediaminetetraacetate precursors and alkali promoters. This resulted in 20-fold improved low-T alkane oxidation rates using H_2O_2, as compared to a standard $Fe(NO_3)_3$ precursor, and an improved understanding of the interplay of synthesis, structure, and function in these supported oxides. Secondly, a manuscript was recently published in *Nature Chemistry*, which described the synthesis of Al_2O_3-on-TiO_2 nanocavities, giving reactant selective oxidations and reductions. This proof of concept report establishes the value of this new approach to catalyst synthesis. In the past year, this same concept is being applied in reverse to nanostructured TiO_2-on-SiO_2 catalysts. Finally, we completed the structural characterization (primarily x-ray absorption and UV-visible spectroscopies) of supported MnOx catalysts derived from precursors of different nuclearities and evaluated their performance in alkane oxidation with O_2. The catalysts derived from the structured precursors gave results characteristic of more-dispersed catalysts than for a typical $Mn(NO_3)_3$ precursor.

Exploration of Surface and Catalysis of Oxide-Based Catalysts Through Operando Approaches

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Funding:	$140,000

PROGRAM SCOPE

Transition metal oxide is one of the most important components of heterogeneous catalysts in chemical transformation and energy conversion. Many of them are reducible oxides. Surface defects such as oxygen vacancies play an important role in catalysis. These defects could be produced during catalysis. Even a phase transformation of reducible oxides could be performed during catalysis. Their catalytic performances can be impacted significantly by surface structure and chemistry of catalysts or phase transformation during catalysis. Both understanding of catalysis from a correlation between surface chemistry and structure of catalysts during catalysis *and* catalytic performance and development of catalysts are goals of this project. In-house ambient pressure x-ray photoelectron spectroscopy using monochromated Al Kα will be used to track surface chemistry of catalysts under reaction condition and during catalysis. An intrinsic correlation between their surface chemistry and structure during catalysis *and* the corresponding catalytic performances will be built. This correlation will provide insights for understanding catalytic performances and developing catalysts.

FY 2012 HIGHLIGHTS

So far, we studied catalytic performance of Co_3O_4 nanorods in the reduction of nitric oxide with carbon monoxide and the corresponding surface chemistry and structure during catalysis or under reaction conditions. An intrinsic correlation between surface chemistry of cobalt oxide and the catalytic selectivity to production of N_2 was built in our studies. The correlation suggested that a new phase, nonstiochoetmric cobalt monoxide, is responsible for a rapid increase of selectivity to production of nitrogen. Based on this insight, we have successfully developed a nonstoichiometric cobalt monoxide catalyst which converts nitric oxide with 100% selectivity to production of nitrogen at a relatively low temperature. In addition, through formation of singly dispersed bimetallic nanoclusters on cobalt oxide surface during catalysis, a new catalyst with high selectivity and activity at a temperature as low as 150^oC was developed. In the next period, we will develop catalysts of cobalt oxide impregnated with metal nanoclusters for generation of hydrogen from methanol. We envision that it will be highly selective in generation of hydrogen in methanol partial oxide through a bi-functional mechanism.

Towards Realistic Reaction Environments in Catalysis Simulation

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Funding:	$155,000

PROGRAM SCOPE

Activation of the O=O molecular bond towards reactions with other molecules is one of the most important of catalytic processes. The detailed mechanisms by which this activation happens, how these mechanisms depend on the structural and compositional details of the material, and in particular how the factors like 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 O_2 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. The catalytic oxidation of NO to NO_2 serves as a relatively simple yet practically important model system, but the implications extend outside this particular context. This research employs high performance computer simulations based on quantum mechanical density functional theory (DFT) to reliably predict chemical structures and reactivity at the molecular scale. The results of these simulations form the basis for higher-level statistical mechanical and chemical kinetic modeling of catalytic reactivity.

FY 2012 HIGHLIGHTS

This year, we extended our quantitative models of catalytic oxidation on Pt(111) in several directions. We demonstrated that the same model can be used to reproduce the temperature programmed desorption of O_2 from Pt—the first time this has been done completely from accurate first principles calculations. We extended the kinetic models to surfaces with steps and kinks—more realistic representations of real catalytic surfaces—and we demonstrated the periodic trends in catalytic oxidation to the other late transition metals. Lastly, we looked carefully at the mechanism of O_2 dissociation on Pt(111) using DFT methods to clarify the connections between the several different pathways that had been proposed in the literature.

Investigation of the Nature of Active Sites on Heteroatom-Containing Carbon Nano-Structures for Oxygen Reduction Reaction

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Funding:	$170,000

PROGRAM SCOPE

This project is an investigation of heteroatom-doped, transition metal-containing nano-structured carbon catalysts for oxygen reduction reaction (ORR) in proton exchange membrane (PEM) fuel cells and direct methanol fuel cells (DMFC). The project targets to understand the nature of ORR active sites and explore ways to create these sites by molecular tailoring of the carbon nano-structures and surface moieties. We have synthesized nitrogen-containing carbon nanostructures (CN_x) by pyrolyzing C- and N-containing precursors over supports doped with a transition metal. These materials are active for ORR in acidic media. We have examined the role of the carbon nano-structure and the nature of nitrogen functional groups in determining the ORR activity. We explored other heteroatoms such as P and S as carbon dopants. We have also investigated the nature and the role of the transition metal in these catalysts by using selective poisons, such CO, H_2S and cyanide as probe molecules. These studies showed no evidence of poisoning of CN_x catalysts, implying that the transition metal does not play a role in catalyzing the ORR in CN_x. More recently, we have characterized the carbon growth process on two different growth substrates using operando X-ray absorption spectroscopy (XAS) at Argonne National Laboratory.

Next, we aim to compare the active sites and mechanisms of deactivation of CN_x to a related class of materials, denoted as Fe-N-C catalysts, which give higher initial activity, but have shown rapid deactivation under fuel cell conditions. One of the main differences between the two catalysts is that CN_x catalysts are acid washed after a heat treatment to remove exposed transition metal and inactive support, whereas Fe-N-C catalysts are not. The iron-phase in these catalysts will be investigated using XAS, transmission electron microscopy, temperature-programed oxidation, and x-ray photoelectron spectroscopy. Stability and activity tests will continue using voltammetry and fuel cell measurements.

FY 2012 HIGHLIGHTS

We have characterized the growth process of CN_x catalysts through acetonitrile pyrolysis using operando XAS. This work was coupled with in-situ x-ray diffraction, high-resolution transmission electron microscopy and X-ray photoelectron spectroscopy and has yielded valuable information about changes occurring in the metal-phase of CN_x with heat treatment, at different stages of acetonitrile pyrolysis, and after acid washing. We also started conducting experiments that elucidate differences between CN_x and Fe-N-C catalysts, which will be completed in the next stage of the project. We designed operando cells that will allow XAS characterization of ORR catalysts during half-cell or fuel cell operations. We have also filed a patent application for the P-doped CNx materials as ORR catalysts.

Mechanistic Studies Aimed at the Development of Single Site Metal Alkoxide Catalysts for the Production of Polyoxygenates from Renewable Resources

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Funding:	$150,000

FY 2012 HIGHLIGHTS

Three major research trusts were the focus of work funded by DOE during the past 12 months: (1) the homopolymerization of propylene oxide (PO) and the copolymerization of PO and CO_2 to form, respectively, polypropylene oxide and polypropylene carbonate by porphyrin-chromium (III) and cobalt (III) initiators; (2) the copolymerization of styrene oxide with carbon dioxide and succinic anhydride to form, respectively, polystyrene carbonate and polystyrene succinate; and (3) the chemistry of magnesium alkyls $LMgBu^{n}(THF)$ and $L'MgBu^{n}(THF)$ complexes where L = the β-diiminate and L' = the methylene dipyrrole ligands shown in I and II, respectively.

Catalytic Deoxydehydration of Carbohydrates and Polyols to Chemicals and Fuels

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Funding:	$146,000

PROGRAM SCOPE

The long term, practical objective of this project is to develop catalytic processes for the deoxydehydration (DODH) of biomass-derived carbohydrates and polyols to produce unsaturated alcohols and hydrocarbons of value as chemical feedstocks and fuels. Achievement of this objective will be enabled through fundamental reactivity studies that will provide new knowledge and a deeper understanding of the ability of oxo-metal complexes (LMO_n) to activate and transform polyhydroxylic substrates.

FY 2012 HIGHLIGHTS

(1) Non-Precious Metal Catalysts for the Glycol-to-Olefin (DODH) Reaction: A number of economical metavanadate salts and polyoxo-vanadium complexes (e.g., (polyamine)VO_2^+, (amine-dicarboxylate) VO_2^-) have been evaluated as catalysts for the DODH of representative glycols, providing the first examples of DODH catalyzed by non-precious metal compounds. With sulfite or PPh_3 as reductants,

moderate to good yields of olefins are obtained with 10 mol% catalyst at 150^{o}C. Catalyst structure/activity correlations are continuing in order to improve activity and selectivity.

Economical molybdate, polyoxomolybdate, and dioxo/trioxo-molybdenum complexes have been evaluated as catalysts for the DODH of representative glycols, providing another set of non-precious metal DODH catalysts with even higher activity. With sulfite or PPh_3 as the reductant, low to good yields of olefins (10-60%) are obtained with 10 mol% catalyst loading at 150^{o}C. The primary by-products are oligomeric ethers from glycol dehydration. The most active DODH system to date is $PPh_3/O_2MoCl_2(DMF)_2$, which can achieve high conversions within a few hours at 100^{o}C.

(2) Development of Effective Systems for the DODH of Higher Polyols: Extending the DODH reaction to higher polyols from biomass is an important project objective. Efforts toward this objective have concentrated on investigating the DODH of xylitol, an abundant sugar alcohol. Employing mainly the sulfite-rhenium oxo systems, we have surveyed a variety of solvent systems (including solvent-free), solubilizing additives, and reaction conditions and have found that low to moderate yields of olefinic or dienyl-alcohols can be produced with good selectivity, depending on the sulfite/xylitol ratio, in mixed aromatic/water systems. The benzyl alcohol(reductant)/NH_4ReO_4 pair is both effective and convenient for product separation and catalyst recovery/recycle.

(3) Computational Analysis of the Sulfite-$MeReO_3$ DODH Catalytic Cycle: To shed light on the details of the DODH catalytic pathway, we are conducting DFT-B3LYP computations to identify viable reaction intermediates, transition states, and their energetics. We are using ethylene glycol, sulfite species, and $MeReO_3$ as the reacting species and are employing a mixed basis set and both gas phase and solvent models. Over 30 different intermediates have been evaluated, and probable transition states for the sulfite reduction and olefin elimination steps have been located.

Influence of Multi-valency, Electrostatics and Molecular Recognition on the Adsorption of Transition Metal Complexes on Metal Oxides: A Molecular Approach to Supported Catalyst Synthesis

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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 of transition metal precursors onto the support surface during catalyst synthesis has received very little attention. We propose to examine 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 TMCs. Novel methods will be utilized to assess the thermodynamics and kinetics of TMC adsorption on neutral and charged interfaces. Isothermal titration calorimetry will quantify the free energy of adsorption of TMCs onto charged metal oxide surfaces and neutral surfaces via adsorption of siloxy-, aqua- and organometallic-based TMCs. In-situ methods to follow the transformation of adsorbed TMCs and their growth into nanoparticles will be followed in real time via synchrotron-based x-ray absorption and scattering. The outcome of this study will represent the first quantitative relationship between TMC adsorption energy on various hydrated supports and the final particle size and/or shape after standard thermal pretreatments. 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 2012 HIGHLIGHTS

We have measured the adsorption energy of two ionic Pt precursors under hydrated conditions over silica and alumina utilized isothermal titration calorimetry over the pH range of 2-12. These initial calorimetry results suggest that electrostatics are alone, not sufficient enough to describe trends in adsorption energy and uptake as a function of pH. It is apparent that the endogenous ligands of the transition metal precursor, while potentially undergoing aquation and ligand exchange reactions, influence the measured adsorption energy and uptake, demonstrating that electrostatics alone cannot explain energetic and reactivity trends. Over the next year, we will correlate the measured adsorption energy under solvated conditions with the propensity for catalysts to sinter under typical pretreatment conditions. These measurements coupled with our initial calorimetry results will be used to test our hypothesis that catalyst stability is influenced significantly (i.e., history effect) by the initial synthetic conditions.

Transition Metal Mediated Transformations of Small Molecules

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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 in the current grant period are (1) the design of metal-catalyzed systems for the synthesis of novel classes of polymers and (2) the identification of new metal-mediated systems for the conversion of biomass to fuels and chemicals. In the first area, we have examined in detail the mechanism of non-alternating copolymerization of ethylene with carbon monoxide catalyzed by a neutral palladium catalyst bearing the phosphine-sulfonate ligand. The copolymer combines the processability of polyethylene with such desirable properties as adhesion, paintability, and hardness. In the area of biomass conversion, we are exploring the catalytic conversion of cellulosic biomass to selected high value products. One target is 2,5-dimethyltetrahydrofuran which is a valuable organic solvent that also has many desirable properties that make it an excellent candidate for gasoline replacement.

FY 2012 HIGHLIGHTS

We have discovered a novel one-step process for the conversion of carbohydrates to furan derivatives mediated 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: it 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.

Fundamental Studies of the Steam Reforming of Alcohols on PdZnO and Co/ZnO Catalysts

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Funding:	$170,000

PROGRAM SCOPE

The goal of this project is to elucidate the relationships between the structure and reactivity of Pd/ZnO, Pt/ZnO, and Co/ZnO alcohol steam reforming catalysts and to determine the origins of the unique reactivity of these catalytic systems. In addition to identifying the relevant reaction pathways and intermediates, the research program is investigating how alloying Pd and Pt with small amounts of Zn alters the selectivity for methanol steam reforming from 100% CO and H_2 to nearly 100% CO_2 and H_2. For Co/ZnO, the active phase of the catalyst is being determined (i.e., Co, CoO, CoZn alloy, etc.) and again the role of the support is being studied. A surface science approach using model single crystal catalysts (e.g., Pd/ZnO(0001), Zn/Pt(111), Co(0001), and Co/ZnO(0001)) and an array of surface sensitive spectroscopic probes (HREELS, XPS, LEED, AES, TPD, AFM) is being used to characterize surface structures and adsorbed intimidates at the molecular level. In addition to determining the mechanisms of alcohol steam reforming reactions, this project is providing fundamental insights that will be useful in understanding the reactivity of a wide range of supported metals catalysts. For example, we are investigating how long-range electronic interactions affect the catalytic properties of “dilute” binary metal alloys (i.e., alloys that contain only a small amount of one of the metals) and the role of catalytic sites at the interface between the metal and a reducible oxide support.

FY 2012 HIGHLIGHTS

We have completed our studies of supported cobalt-based ethanol steam reforming catalysts. Our work shows that the high activity observed for Co on reducible supports is due to the fact that these supports facilitate the oxidative dehydrogenation of ethoxide to acetaldehyde by providing the oxygen required for this reaction. This pathway results in reduction of the support, which is then reoxidized via reaction with water in a subsequent step. Our results also show that in addition to promoting this reaction, the facile transfer of oxygen from the support to the Co plays a role in removing carbon deposits and thereby helps maintain activity. We also initiated studies of how alloying Pt with Zn alters the selectivity for the steam reforming of ethanol to produce H_2 and CO_2. In our initial work in this area, we mapped out the structure of Pt(111) surfaces decorated with submonolayer amounts of Zn and the structure of PtZn near surface alloys. The effect of alloying with Zn on the heat of adsorption of CO has been measured, and studies of the effect alloying on the energetics of C-H, C-C, and C-O bond scission in adsorbed ethoxide groups have been initiated.

Thermodynamic Properties of Supported Catalysts

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Funding:	$170,000

PROGRAM SCOPE

The goals of this program are to understand (1) how support and composition affect the thermodynamic properties for oxidation and reduction of various oxide and metal catalysts, and (2) how redox properties at a surface differ from that of bulk materials. The thermodynamic properties for oxidation and reduction of bulk materials are well known. However, typical catalytic materials are in the form of nano-particles, supported on high-surface-area oxides, and often in the form of a mixed oxide or solid solution. The redox properties of these types of materials are not usually known in detail. For selective oxidation reactions which proceed by a Mars-Van Krevelen mechanism, understanding the redox properties of the catalyst is critical to a fundamental understanding of the reaction and to the development of new and improved catalysts. For reactions involving steam or CO_2, the thermodynamic properties of the catalyst affect the oxidation state of the catalyst under steady-state reaction conditions, thereby affecting the activity and selectivity of the reaction.

FY 2012 HIGHLIGHTS

Supported Co: It has been suggested that the Co catalysts used in Fischer-Tropsch Synthesis (FTS) can be oxidized under FTS conditions even though bulk thermodynamics would suggest that Co should remain metallic. Using coulometric titration, we have demonstrated that the redox properties of Co particles as small as 4.5 nm are indistinguishable from that found for bulk Co. However, there is evidence for interactions with zirconia that shift the equilibrium $P(O_2)$ to lower values. These interactions can be removed by the addition of dopant levels of Pd, perhaps because the precious metals segregate to the interface between the Co and the support.

Core-Shell Catalysts: We have developed a novel method for preparing M@oxide (M = Pt, Pd; oxide = ceria, zirconia, or titania) nanoparticles in solution, then attaching these particles onto functionalized supports. Pd@ceria/alumina catalysts prepared in this way exhibit exceptional activity for methane oxidation and remarkable stability against sintering. For catalysts calcined at lower temperatures (500°C), the ceria shell can undergo reduction easily, leading to low activities for steam-reforming and water-gas shift reactions due to “closing” of the shell around the Pd particles. However, calcination at higher temperatures (800°C) leads to catalysts that are very active and stable under reforming conditions.

Understanding, Harnessing, and Tuning the Catalytic Chemistry of Nonstoichiometric Oxide Surfaces

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Funding:	$170,000

PROGRAM SCOPE

The main goals of this project are the study of catalysis on known nonstoichiometric surfaces, the discovery of new nonstoichiometric surfaces guided by understanding how changes in surface composition affect surface reactivity, exploration of the catalytic properties of the newly-discovered surfaces, and the development of new nonstoichiometric oxide surfaces incorporating catalytic and base metal atoms to enhance catalysis.

FY 2012 HIGHLIGHTS

Through an *ab initio* investigation, we predict the enhancement of the oxygen evolving activity of a Ti^{IV}-based perovskite, $SrTiO_3$, via surface structure modification. We predict that a reconstructed surface of $SrTiO_3$ will have activity comparable with IrO_2, one of the best heterogeneous water oxidation catalysts.

We have developed a rigorous procedure for electron partitioning among atoms in extended systems based on wave-function topology and the modern theory of polarization.

We showed, using density functional theory calculations, that the low-energy epitaxial $PbTiO_3$ (001)/Pt interface strengthens electrode-oxide bonds by breaking in-plane symmetry and stabilizes a ground state with enhanced polarization in sub-nanometer oxide films, with no critical-size limit.

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

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Funding:	$220,000

PROGRAM SCOPE

The ultimate objective of this research project is to gain fundamental knowledge about the relation between surface composition and catalytic performance of metallic alloy catalysts through first-principles based multi-scale simulations. The surface composition of catalyst clusters are determined by many interplaying effects (such as chemical composition, crystal structure, particle shape/size, and reduction temperature) related to their synthesis process. In addition, chemical reaction conditions (such as gas species, solution, and temperature) could modify the surface composition of alloy catalysts. The performance of catalysts refers to their capability to selectively and actively promote some given chemical reactions. Therefore, this study will fill existing knowledge gap between the fabrication process and the resultant functionality (and/or stability) of alloy catalysts. This study focuses on theoretically investigating oxygen reduction reaction (ORR) on multi-component Pt alloy surfaces. Consequently, one specific objective of the proposed research is to provide design principles for developing low-cost, high-performance, and long-durability electrocatalysts for polymer electrolyte membrane fuel cells. Another specific objective of the proposed research is to enhance our capability in synergistically coupling multi-scale, multi-paradigm, and multi-resolution predictive models for catalyst design.

FY 2012 HIGHLIGHTS

(1) We have developed the modified embedded atom method (MEAM) atomic interaction potentials for 10 kinds of binary alloys (Pt-Ni, Pt-Re, Pt-Mo, Pt-Ti, Pt-Pd, Pt-Fe, Pt-Co, Pt-Mn, Pt-V, and Pt-Au) and 3 kinds of ternary alloys (Pt-Ni-Co, Pt-Fe-Ni, and Pt-Pd-Ni). Moreover, we examined that the surface segregation in these Pt alloys was able to be accurately predicted with the developed MEAM potentials and the Monte Carlo simulation method.

(2) We have performed the first-principles transition state study on oxygen reduction reaction (ORR) on the (111) and (100) surfaces of pure Pt and Pt-Ni alloy. It was found that the ORR proceed through oxygen dissociation mechanism on the Pt (111), Pt(100), and Pt/Ni (100) surfaces while through hydrogen peroxide dissociation mechanism on the Pt/Ni (111) surface.

(3) We have developed a kinetic Monte Carlo simulation code to simulate the kinetics of ORR on the surface of pure Pt and Pt/Ni alloy surfaces.

Understanding Nitrogen Fixation

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PROGRAM SCOPE

The goal of our DOE-funded program is to develop methods for the conversion of molecular nitrogen (N_2) into more value-added nitrogen-containing compounds used as fuels, fertilizers, fine chemicals, and materials. Specifically, we seek to develop ammonia independent routes to organic molecules thereby reducing the fossil fuel demands and CO_2 byproducts associated with the Haber-Bosch process. At the core of our effort is the discovery of new methods for the synthesis of nitrogen-carbon bonds. Our approach has exploited the chemistry of reduced group 4 transition metal complexes that are highly effective for activating the kinetically and thermodynamically inert N≡N bond. By providing four of the six requisite electrons required for N_2 cleavage, we have discovered a host of dinitrogen functionalization and even cleavage reactions. Specifically, we have forwarded the concept of “ligand-induced” N_2 functionalization and cleavage whereby the metal center and the external reagents work in concert to provide both the reducing equivalents and the substrate for new nitrogen-element bond formation.

FY 2012 HIGHLIGHTS

We have continued to explore early transition metals for the activation and subsequent functionalization of atmospheric nitrogen. We have increased attention to titanium dinitrogen chemistry as this metal offers properties most compatible with catalytic turnover. Specifically, we have synthesized titanium compounds with more open cyclopentadienyl ligands in an effort to produce highly activated N_2 complexes, which should be poised to undergo N-C bond forming reactions. These efforts produced a trinuclear complex with the most activated N-N bond observed in titanocene chemistry. We have also continued our studies into N-C bond-forming reactions between N_2 and carbon monoxide promoted by zirconium and hafnium compounds. Kinetic, isotopic labeling and spectroscopic studies were used to identify an important reaction intermediate that contained three CO molecules, an unexpected finding as the final product only incorporates two equivalents of carbon monoxide. The intermediate was intercepted with carbon electrophiles and heterocummulenes such as carbon monoxide, resulting in both N_2 splitting and CO homologation. Both reactions are important to understand in the context of energy efficient N_2 fixation and the synthesis of organic molecules by Fischer-Tropsch-type chemistry. As part of these studies, we also synthesized a new hafnocene dinitrogen complex with sterically unencumbered 1,2,4-trimethylcyclopentadienyl ligands. Addition of carbon monoxide to this compound resulted in isolation and full characterization of the first hafnium nitride complex prepared from N_2 cleavage. This result is a significant breakthrough in our understanding of ligand-induced dinitrogen cleavage and opens many new opportunities for functionalization of the dinitrogen molecule under mild conditions in solution. In the current funding period, we are studying the reactivity of this species including new examples of cycloaddition chemistry as well as establishing its fundamental chemistry and ability to act as both a base and a nucleophile.

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

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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 to (1) determine the structure and reactivity of oxidized and reduced TiO_2 surfaces and interfaces, (2) understand the behavior of photoexcited electrons and holes at TiO_2 surfaces and TiO_2-water interfaces, and (3) extend the knowledge gained for TiO_2 to other promising (photo-)catalytic metal oxides, particularly cobalt oxides.

FY 2012 HIGHLIGHTS

We studied the dynamics of surface oxygen vacancies (Vo's) created by electron bombardment at low temperature on anatase TiO2 (101) using STM measurements and first principles calculations. We found that the surface Vo's start migrating to subsurface sites at temperatures ≥ 200 K. After an initial decrease of the Vo density, a temperature-dependent dynamic equilibrium is established where Vo's move to subsurface sites and back again. We estimate that activation energies for subsurface migration lie between 0.6 and 1.2 eV, consistent with the theoretically predicted barrier of ~ 0.75 eV. The wide scatter of the experimental estimates may be attributed to inhomogeneously-distributed subsurface defects in the reduced sample.

We studied the adsorption and oxidation of water on the (110) surface of the spinel cobalt oxide Co_3O_4, a widely used oxidation catalyst. The computed free energy changes along the oxygen evolution reaction show that the rate limiting step of the reaction is the second water deprotonation. An upper bound estimate of the proton transfer barrier indicates that its effect on the overpotential is small.

Catalyst Design by Discovery Informatics

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Funding:	$780,000

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 the 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; while for homogeneous catalysis, it is single site olefin polymerization.

FY 2012 HIGHLIGHTS

Our previous work on WGS has revealed the importance of the catalyst support for water activation and has shown, for Au/TiO_2 catalysts, that the corner atoms of Au cubooctohedral particles are active sites for WGS. To further examine support contributions to WGS, we have been studying the effects of alkali promotion, examining multiwall carbon nanotubes (MWCNT) as supports, and varying the metal support ratio. With detailed steady state and ^{13}CO isotopic switch kinetic experiments, supported by TEM, XPS, and *operando* FTIR catalyst characterization, we have shown that Na promotes Pt/Al_2O_3, Pt/TiO_2, and Pt/MWCNT by assisting in water activation. In all cases, Na is associated with a signature change in kinetics to increased water order and apparent activation energy; and the Pt is in the metallic state. Assignment of water activation to the support was further confirmed with Pt/ZrO_2 catalysts at ~76wt%Pt loading prepared by atomic layer deposition. In this case the metal covered most of the support sites, thus blocking the support function and lowering the rate. In order to widen the chemistry space, we have added metal-promoted Mo_2C to our catalyst library. Kinetic studies have identified the adsorption strength of CO as a descriptor of the promoting metal activity. These catalysts are also bi-functional, with both the metal and the support surface playing a vital role in the generation of high activity for the WGS reaction. Modeling to identify descriptors of the support function and the chemistry at the metal support interface in WGS is in progress.

Using robust data sets that include molecular weight distributions (MWD) and end group analysis, together with a detailed population balance approach that can model the MWD, we have been examining effects of structure on individual rate constants for a family of Salan-type Zr and Hf catalysts. We have found a lowering of the propagation rate constant when Hf is substituted for Zr and pendant group effects on chain transfer rate constants that correlate with Zr-ligand bond length. Further work on electronic and steric effects on specific rate constants and associated structure-property relations is underway. A new Dynamic Monte-Carlo Polymerization simulator has been developed to handle more complex mechanisms, including ring opening polymerization of caprolactone.

Fundamental Studies of Oxidation Reactions on Model Catalysts

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Funding:	$146,000

PROGRAM SCOPE

The goal of this research is to gain a fundamental understanding of the underlying chemical descriptors in catalytic oxidation reactions on metals. To study these effects, we have chosen the partial oxidation of propylene on Au/titanium silicalite-1 (TS-1) as a model reaction. The nano-sized gold particles in this system catalyze H_2 and O_2 to form hydrogen peroxide, an environmentally benign oxidant, which is subsequently used by the Ti sites of TS-1 to produce propylene oxide (PO). Our previous research has shown that catalyst preparation conditions affect the size of Au nano-particles, significantly impacting catalytic performance. We propose that the active Au clusters for PO synthesis are sufficiently small ($d_p < 1$ nm) to be located inside of the TS-1 nano-pores.

In this research program, we will utilize a combination of reaction kinetics and catalyst characterization techniques to identify the nature of active Au species in Au/TS-1 catalysts for propylene partial oxidation. Through steady-state and transient kinetic measurements, we can obtain powerful information regarding the partial oxidation reaction mechanism, monitor changes in the rate-limiting step, and determine the individual kinetic parameters including apparent activation energies and reaction orders. Understanding and controlling this system at the molecular scale promises not only further enhancement of reaction rates and product selectivity, but also new concepts that can be applied to other nano-particle catalyst systems.

FY 2012 HIGHLIGHTS

We investigated the effect of catalyst preparation conditions on catalytic performance and developed better control of catalyst reproducibility for PO synthesis. Additionally, by using a specially designed silicalite-1 (S-1) coating on top of the TS-1 support, we have shown that small Au clusters ($d_p < 1$ nm), presumably inside of the TS-1 nano-pores, are the active species for PO synthesis. The S-1 coating on the external catalyst surface exhibits the same pore structure as TS-1, except that it does not contain Ti sites. Therefore, any active Au species in close proximity to the Ti sites required to produce PO must be located within the TS-1 nano-pores.

Oxo Catalyst for the Conversion of Lignocellulosic Biomass

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Funding:	$155,000

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 CO_2, H_2O, and sunlight to make lingocellulosic 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. Our guiding principle is to start with metal oxo catalysts that are known to affect oxygen atom transfer and devise reaction pathways that would remove oxygen from biomass derived polyols. 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 a secondary alcohol as the reductant. We will extend the MTO-catalyzed reaction to biomass derived glycerol and polyols to make alkenes and high value organics (HVOs) that can be used as drop in chemicals in polymer synthesis. Our proposed research has the advantage of employing cheap secondary alcohols and avoids the use of hazardous hydrogen and high pressure. The kinetics and mechanism of the MTO-catalyzed deoxygenation reaction will be defined to aid in the design of new catalysts. The broad impact of this work will be to develop green technologies to provide drop in chemicals from cellulosic biomass.

FY 2012 HIGHLIGHTS

We have successfully demonstrated the use of MTO as a catalyst under neat conditions for the conversion of glycerol selectively to allylic alcohol and 1,3-dihydroxyacetone (DHA) at 165 °C. In this reaction, the substrate glycerol acts as the reductant. In other words, half of the glycerol is deoxygenated to allylic alcohol, which is volatile and collected as it is being produced, and half of the glycerol is dehydrogenated selectively to DHA, which remains in the reaction flask residue as it is not volatile. DHA is used in spray tanning solutions. If a secondary alcohol such as 3-octanol is used under these conditions, MTO catalyzes the conversion of glycerol to > 90% yield of allylic alcohol. An attractive feature that is built into this catalytic process is the easy separation of the product, which allows for catalyst recycling.

We have also completed a detailed kinetic study on the MTO-catalyzed deoxygenation of vicinal diols by secondary alcohols. The rate is half order in [catalyst] and zero order in [diol]. NMR studies under relevant catalytic conditions revealed the identity of several reaction intermediates. We have been able to formulate the most productive catalytic cycle and identify the key rhenium diolate intermediates. In the next period, we envision combining our mechanistic understanding with computational design tools to expand this to abundant and more robust metal catalysts.

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

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PROGRAM SCOPE

We have completed the development of the database of zeolite-like materials. This database contains on the order of 2.6 M unique structures, roughly 15% of which have formation energies within 30 kJ/mol Si of α–quartz, the band in which the known high-silica zeolites exist. These structures have topological, geometrical, and diffraction characteristics that are similar to those of known zeolites. The database is the result of refinement by two interatomic potentials that satisfy the Pauli exclusion principle. The database is available upon request and has been deposited in the publicly available PCOD database and at http://www.hypotheticalzeolites.net/database/deem/.

We are developing a procedure to identify organic structure directing agents (OSDAs) that are predicted to aid the synthesis of a specific zeolite. The zeolite can be a known one for which synthesis is to be optimized, or the zeolite can be a predicted one from our database of 330,000 structures. We use a genetic algorithm to build candidate OSDAs from a library of commercially available compounds. We will build molecules from known chemical transformations upon these fragments. In this way, the candidate OSDAs are chemically accessible.

FY 2012 HIGHLIGHTS

The database has been published [*Phys. Chem. Chem. Phys.* 13, 2011, 12407]. The database of predicted zeolite structures has been screened for CO_2 adsorption capacity [*Nature Materials* 11, 2012, 633]. The parasitic energy to separate CO_2 from flu gas has been calculated for all structures. The optimal set of structures as a function of Henry's coefficient was identified. Several novel zeolites are superior to all known zeolites, and the best zeolites have a ~30% lower parasitic energy than does the near-term amine capture technology. We have also developed several new thermostat simulation methods to sample complex free energy landscapes.

Activation and Functionalization of Carbon-Hydrogen and Carbon-Carbon Bonds

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PROGRAM SCOPE

Our research is now examining the activation of C–H bonds in substituted hydrocarbons and the cleavage of carbon-carbon bonds in alkynes and nitriles. These projects have involved a variety of fundamental studies of model reactions, as well as actual catalysis. Expansion of the scope of substrates now includes sp-hybridized C-H bonds as well as substituted hydrocarbons (CH_3-X, x = benzyl, allyl, F, Cl, CN, OMe, O-*t*-Bu, C≡CMe, C(=O)Me, CF_3). Determination of the relative metal-carbon bond strengths in these compounds provides deep insight into the factors controlling the kinetics and thermodynamics of C-H bond activation.

FY 2012 HIGHLIGHTS

Our recent work in C–H activation has provided insight into the dilemma concerning the well-established greater stabilities of metal-carbon bonds when an electron-withdrawing substituent is present; these compounds appear to be thousands of times more stable than their unsubstituted counterparts, yet all prior chemical knowledge would indicate that these metal-carbon bonds should be weaker, not stronger. Our thermodyanmic analysis gives the answer: the bonds are indeed weaker in the substituted derivatives, but they are not as weak as one would anticipate and therefore, the compounds appear to have greater stability.

Our work in C–C bond activation is groundbreaking in that these types of reactions are almost unknown. We have found a large variety of examples of cleavage of a particular type of C–C bond, the carbon-nitrile bond, and can thoroughly account for the factors that are necessary for its cleavage. Our work has stimulated others to use this discovery in applications for the synthesis of complex chiral compounds of pharamceutical interest in one step.

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

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PROGRAM SCOPE

The overall research goal of this project is the development and validation of highly efficient and accurate computational methods for predicting the elementary reaction rates of processes occurring at solid-liquid interfaces relevant for the conversion of lignocellulosic biomass model molecules. Furthermore, we aim at identifying the importance of an aqueous reaction environment on reaction mechanisms, activity, and selectivity for the C-O versus C-C bond cleavage in ethylene glycol and glycerol, and reductive deoxygenation versus hydrogenation of guaiacol over Pt (111) model catalyst surfaces. Specifically, we have developed an explicit hybrid (QM/MM) solvation model for solid surfaces (*eSMS*) that is based on our subtraction scheme for metals and the QM/MM-MFEP methodology developed by Yang et al. for homogeneous and enzyme catalysis. In addition, we extended our research idea of the *eSMS* methodology to the development of an implicit solvation model for solid surfaces (*iSMS*). Finally, we started applying and validating our computational methodologies to the reductive deoxygenation of ethylene glycol, glycerol, and guaiacol on Pt (111) model surfaces.

FY 2012 HIGHLIGHTS

Thus far, we have successfully demonstrated that although the electrostatic interaction of liquid water with adsorbed reactants is long-ranged, the effect of water on the bonding characteristic of transition metal surfaces with adsorbates is short-ranged. As a result, rapid convergence of the *eSMS* and *iSMS* methodologies can be expected and is indeed observed in all test calculations. Next, we note that the *iSMS* methodology will, for the first time, permit the application of highly optimized implicit solvation models developed in the past one to two decades to reactions on solid transition metal surfaces described by plane wave density functional theory. Consequently, it will become possible to (1) study the approximate effect of a solvent on elementary reaction rates of processes occurring at a solid-liquid interface and (2) rapidly screen solvents *in silico* for heterogeneous catalysis applications.

Photocatalysis of Modified Transition Metal Oxide Surfaces

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PROGRAM SCOPE

Sunlight is the most abundant energy source. In order to tap into this resource, more efficient ways for converting solar energy into other forms of energy that can be stored and transported is needed. Harvesting sunlight and converting it into chemical fuels is one promising approach to reach the goal of a sustainable energy source. Photocatalysts absorb light and use the generated electron-hole pairs to perform redox reactions on molecules adsorbed at their surfaces. In this way, for example, hydrogen can be produced from hydrocarbons or even water. Currently used photocatalysts, such as TiO_2, lack in their efficiency to be viable for an economic energy production. In order to increase their activity, these materials need to be modified and their surfaces need to be engineered in order to possess appropriate functionalities. In this proposal, we investigate the fundamental principles and suggest new approaches to make transition metal oxides more effective photocatalysts. The knowledge gained from the proposed experiments will aid the controlled design of materials with increased photochemical surface reactivity.

We will perform studies primarily on single crystalline materials under ultra high vacuum conditions. This enables us to characterize surfaces and to modify them in a controlled manner. We will use multiple surface science techniques to characterize the surface geometrical and electronic structure. Furthermore, the chemical surface properties and the photocatalytic properties are being measured. This approach enables us to determine physical materials properties and to correlate them with their (photo)chemical activity. With these experimental developments, we will address diverse issues in photocatalysis such as the following.

- Surface defects – *What is the importance of surface defects, in particular monoatomic height step edges, for promoting photocatalytic reactions?*
- Loading of photocatalysts with noble metals – *What is the metal-cluster size dependence on the activation of photocatalysts?*
- Surface functionalities of intrinsic surfaces – *Do different crystallographic orientations of the same material exhibit different photocatalytic functions and why?*
- Modification of the surface properties by grafting a monolayer film in order to increase charge trapping at the surface – *Can we enhance charge separation and trapping by controlled surface engineering?*
- Increasing the visible light absorption by bulk doping – *How is the materials chemistry of defect formation in doped materials related to the photochemical surface properties?*

The fundamental understanding of these processes is necessary to design next-generation photocatalysts where several components with different functionalities will act in accord to achieve high efficiencies. The functions of these components will be largely determined by the surfaces and interfaces that join them together at the nanoscale. Thus this proposal will help to define the design-principles for future photocatalytically active materials.

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

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PROGRAM SCOPE

In the field of catalysis, there are three primary metrics by which catalyst materials are judged: activity, selectivity, and stability. Improving any one (or more) of these metrics can provide for significant enhancements in process efficiency with global-scale impact. In this project, we are engaging fundamental studies of catalyst materials for key electrochemical energy conversion reactions involving H_2O, O_2, and CO_2. Two reactions we aim to explore are the oxygen reduction reaction (ORR) and the CO_2 reduction reaction (CO_2RR). The overarching goal is to understand the fundamental factors that govern activity, selectivity, and stability of electrocatalysts for these reactions, and then utilize that insight to develop improved materials. We aim to do so by designing and tailoring the surface structure and interfacial properties of catalyst materials at the nano- and atomic-scale, directly in-line with the Grand Challenge in Catalysis Science as described in DOE's "Basic Needs Report for Catalysis in Energy."

FY 2012 HIGHLIGHTS

We have just recently started this project in September 2012. We have commenced this project by preparing ordered, mesoporous thin-film ORR catalysts consisting of Pt_xNi_{1-x} alloys. Our previous work on ordered, mesoporous thin films of pure Pt with pore sizes on the order of 4-7 nm indicated that high activity and stability for the ORR can be achieved, competitive with state-of-the-art commercial fuel cell catalysts. Key to this improvement was the atomic-scale surface structure that was produced as a direct result of the nano-structured, porous thin films. This morphology engendered different types of surface sites than the ones found on conventional nanoparticle structures. Our initial results suggest that a Pt_xNi_{1-x} alloy with the same meso structure and thus similar surface structure as that of pure Pt may provide added benefit by tailoring the electronic structure of the Pt. We have begun synthesizing this material with the correct mesoporous architecture, and we look forward to reporting on our findings in our next communication.

Enabling Catalytic Strategies for Biomass Conversion

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Funding: $160,000

PROGRAM SCOPE

The goal of this project is to develop an integrated platform of selective catalysts for converting biomass-derived feedstocks into value-added chemicals and polymers. This approach entails the synthesis of monomers that can be polymerized to thermoplastics that can replace existing thermoplastics with competitive materials derived from biomass. This program leverages advances from our laboratories in the development of catalytic platforms for the conversion of bio-derived feedstocks such as lactones and carbonates into value-added polymers, and recent advances from our labs in selective catalytic oxidative transformations of biomass-derived alcohols. We have developed a selective catalytic oxidation of polyols to hydroxyketones; the selective oxidation of glycerol provides a strategy for converting glycerol into new classes of chemical intermediates and polymers. The use of glycerol as a feedstock for renewable polymeric material would offer new possibilities for replacing current materials derived from petroleum. These considerations stimulated our efforts to develop new catalytic processes for the selective oxidation of glycerol to dihydroxyacetone and the catalytic synthesis of cyclic dihydroxyacetone carbonates from the corresponding 1,3-diols. The ring-opening polymerization of cyclic dihydroxyacetone carbonate would provide a new strategy for the synthesis of poly(dihydroxyacetone carbonate) (pDHAC). We were attracted to these polycarbonates due to their structural similarity to the petroleum-derived alternating copolymer of ethylene and carbon monoxide (Carilon™). We posited that the structurally related polycarbonates might exhibit similar properties and thus provide a class of high-melting thermoplastics derived from biomass feedstocks.

FY 2012 HIGHLIGHTS

We have so far developed a new synthetic strategy for the synthesis of high melting polycarbonates from glycerol, a readily available feedstock. Chemoselective catalytic oxidation of glycerol affords dihydroxyacetone; catalytic oxidative carbonylation of dihydroxyacetone yields cyclic dihydroxyacetone carbonate. The ring-opening polymerization of cyclic dihydroxyacetone carbonate with organic catalysts in solution or in the melt affords poly(dihydroxyacetone carbonate) after removal of the acetal protecting groups. We have shown that this material is a high melting thermoplastic with thermal properties comparable to the structurally related ethylene/carbon monoxide alternating copolymers. This synthetic method provides a strategy for the generation of new classes of performance plastics derived from biomass.

We have also developed new catalysts for the oxidative carbonylation of diols to lactones; oxidation of diethylene glycol yields the cyclic monomer para-dioxanone (PDX). Preliminary results have shown that the ring-opening polymerization of PDX can be carried out with organic catalysts to generate poly-PDX, a biodegradable polymer with biomedical applications. We have expanded the catalytic oxidative lactonization reaction to analogous n-Boc and benzyl substituted amino-diols. We anticipate that the resulting delta-lactones will be a versatile class of monomers.

Modeling Catalyzed Growth of Single-Wall Carbon Nanotubes

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PROGRAM SCOPE

Single-walled 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 previous work, we have 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 (i.e., favoring a template effect). Currently we focus on elucidating further aspects of the growth mechanism, such as the effect of 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 2012 HIGHLIGHTS

We have identified carbon atoms involved in surface diffusion, bulk diffusion, and potential carbide formation. Transitions between induction, nucleation, and growth were found to be defined by saturation of the nanoparticle and by changes in the catalytic regime. It was found that carbon nucleation and dissolution may occur simultaneously, with pre-saturation nucleation driven by the low-energy barrier for surface diffusion. Thus for carbon-philic catalysts, induction and nucleation periods are usually governed by bulk diffusion while the growth period is dominated by surface diffusion. Surface diffusion control during growth is in agreement with successful nanotube growth on metals such as copper and gold, which do not dissolve carbon. In the range studied, C solubility decreases with particle size, and the Ni/C ratios found coincide with stoichiometries of known Ni carbides.

New Horizons in C-F Activation by Main Group Electrophiles

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Funding: $143,000

PROGRAM SCOPE

This project expands a novel approach to activation and functionalization of C-F bonds. Our chemistry utilizes highly reactive main group cations (silylium R_3Si^+ or alumenium R_2Al^+), or their closest approximation in solution, that engage 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). Carbon-fluorine bonds are among the most robust functionalities in chemistry owing to their thermodynamic stability and kinetic inertness. 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 as aluminum, magnesium, and semiconductor production. We especially target improvements in the catalyst/reagent cost and in reactivity towards polyfluorinated substrates.

FY 2012 HIGHLIGHTS

One of our foci continued to be on the improvements in the synthesis of weakly coordinating carborane and dodecaborate anions that are essential to unlocking the remarkable reactivity of silylium and alumenium C-F activation catalysts. We have now developed new, convenient syntheses of robust polyhalogenated carboranes that possess increased solubility. We have accomplished this by introducing either an alkyl substituent at the C-vertex of a carborane, e.g., $[Alkyl\text{-}CB11Cl11]^-$ anions, or a triflyloxy substituent on the B vertex, e.g., $[HCB11Cl10(O_3SCF_3)]^-$ anion. These anions allow solubilization of the reactive silylium salts in less polar and less coordinating solvents, paving the way for higher HDF/AlkDF reactivity. Most recently, we have developed a remarkable zwitterionic silylium molecule, which is comprised of a silylium center covalently linked to the carborane anionic core. It displays the structure and reactivity of silylium “salts” but in a single-component, molecular mode.

We have also explored alternative stoichiometric Si-H sourced for HDF. We originally used Et_3SiH and similar trialkylsilanes. We discovered that the much cheaper polymethylsiloxane $(\text{-MeSiHO-})_n$ can function as a stoichiometric source of H. However, its use is complicated by the significant redistribution reactions of the polymer catalyzed by silylium sources. We encountered similar difficulties in the use of other heteroatom-substituted silanes (Me_2SiHCl, $(Me_2N)_3SiH$, $Me_2(MeO)SiH$, etc.).

The Physical and Chemical Properties of Nanostructured Mixed-Metal Catalysts

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Funding:	$220,000

PROGRAM SCOPE

The main targets of this study have been to synthesize well-defined nanoclusters of Pt, Ni, Rh, and Pd as well as mixed-metal nanoclusters on ultrathin oxide surfaces and to characterize their detailed morphology using scanning probe techniques. The focus of the research is an understanding of the effects of metal-substrate interactions and overall composition on the structure/stability of single metal and mixed-metal nanoclusters and their catalytic activity.

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 2013 GOALS

The primary goal for the coming year will be the synthesis of well-defined nanoclusters of Ni-Au on ultrathin oxide surfaces and characterization of their detailed morphology using scanning probe techniques under both UHV and real catalytic conditions. A key target is an understanding of the effects of metal-substrate interactions and overall composition on the structure and stability and catalytic activity of nanoclusters. Work will be initiated to determine the relationship between the size/composition of the nanoparticles and their catalytic activities and selectivities for the reactions.

Theory-Guided Design of Nanoscale Multi-Metallic Catalysts for Fuel Cells

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PROGRAM SCOPE

In past years, we have focused our research efforts on the understanding of activity and durability issues associated with platinum and platinum-based alloy electrocatalysts for the oxygen reduction reaction taking place in acid medium. We have also invested considerable time and efforts in the development of new methods and procedures that help us to perform deeper analyses and to concatenate first-principles techniques, thus bridging results from distinct length and time scales and those of experiments. For example, our studies have evolved from analysis of reactivity in simplified model systems to the inclusion of solvent and acid species and electrochemical potential effects, and to the analysis of side reactions such as that of metal dissolution and the effect of the presence of less-noble elements in the alloy composition, with their associated issues of surface segregation and surface dissolution. Within this theme, we have identified the surface oxidation (and reduction) reactions as key elements to understanding the evolution of the catalytic structure and its long-time behavior.

FY 2012 HIGHLIGHTS

We found density-functional theory-based correlations between surface segregation and the oxidation state of the subsurface atoms, and their effects on metal dissolution. Since the onset of Pt dissolution coincides with that of surface oxidation, surface reconstruction phenomena was evaluated using *ab initio* and classical molecular dynamics at increasing degrees of oxidation on extended surfaces and nanoparticles, including the effects of water and an acidic solution. Significant reconstruction and compositional changes were observed as the surface is modified by the presence of adsorbates and electrolyte components. Kinetic Monte Carlo simulations of nanoparticles helped elucidate dealloying processes. Further analysis suggested an explanation for the enhanced activity observed experimentally in the resultant nanoporous structures.

Correlation of Theory and Function in Well-Defined Bimetallic Electrocatalysts

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PROGRAM SCOPE

The objective of this research is to correlate the structural and catalytic properties of dendrimer encapsulated nanoparticles (DENs) with analogous density functional theory (DFT) simulations. DENs are nanoparticles that are synthesized within poly(amidoamine) dendrimer templates and typically are comprised of 50 to 200 atoms. This size range is small enough to perform DFT calculations of particle structure and to probe catalytic activity of such particles through a combined experimental/theoretical approach. Our key goals are to (1) improve theoretical modeling techniques through our ability to verify theoretical predictions and fine-tune methods and (2) improve synthetic and characterization methods of nanoparticles in the 50 to 200 atom size range for more accurate comparisons with theoretical structures.

FY 2012 HIGHLIGHTS

We have made significant advances toward both of the goals stated above. We have produced experimental results to verify theoretical models on the activity of Pt and Au@Pt particles for formic acid oxidation, the activity of AuPd alloy core@Pt shell particles for the oxygen reduction reaction (ORR), and the structure and ORR activity of Au@Pt nanoparticles. Additionally, we have developed new, more precise synthesis techniques for 147 atom Au DENs and Pd@Pt DENs of various sizes. These new synthetic methods allow us to make very accurate comparisons of experimental results to theoretical studies. For example, a combined extended x-ray absorption fine structure (EXAFS)/theory study has demonstrated that when $Pd_{147}@Pt_{162}$ or $Pd_{55}@Pt_{92}$ DENs are prepared by a new solution synthesis method, they spontaneously rearrange into inverted core@shell structures. This experimental result was confirmed with DFT calculations. Another aspect of our recent work is to develop new computational techniques for the simulation of theoretical EXAFS spectra that can be compared with experimental results. We have demonstrated good agreement between experimental and theoretical EXAFS signals taken from DFT-MD simulations of Au_{147} nanoparticles with varying numbers of surface thiols per particle. This methodology can be very valuable for extracting more accurate nanoparticle structural information from a standard EXAFS signal than the traditional coordination number, bond length, and bond disorder terms and is the future of EXAFS analysis.

Surface Chemistry of Gold Model Catalysts

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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 are considering two major surface catalytic themes regarding the chemistry of these model gold surfaces that build on our experience from the recent past: (1) reactions of adsorbed hydrogen atoms with other relevant molecules on single crystalline gold samples in an ultrahigh vacuum environment and (2) 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 as under ultrahigh vacuum conditions. We have physically characterized these model catalyst surfaces employing several surface sensitive tools. For chemical characterization, we are employing molecular beam surface scattering techniques, temperature programmed reaction spectroscopy, infra-red vibrational spectroscopy, density functional theory calculations (via collaboration with Professors Graeme Henkelman and Gyeong Hwang), and higher pressure (1-100 Torr) batch catalytic measurements on our gold model catalyst surfaces. We have synthesized our inverse model gold catalyst surfaces employing a simple reactive physical vapor deposition technique on the Au(111) substrate.

FY 2012 HIGHLIGHTS

By employing propionaldehyde and acetone as representative probe molecules of aldehydes and ketones, respectively, we investigated the hydrogenation of C=O bonds on a model pre-atomic-hydrogen-covered Au(111) catalyst. H atoms were used owing to the high energetic barrier of H_2 dissociation on gold. Temperature-programmed-desorption measurements indicated different activities for hydrogenation on gold: propionaldehyde underwent hydrogenation to afford 1-propanol on H-covered gold, but acetone did not form 2-propanol. Density functional theory calculations revealed different activation energies for the reactions between a single carbonyl moiety and a H atom.

CO oxidation was studied at pressures between 4 and 100 Torr and temperatures from 400 to 670 K on inverse model catalysts made of Fe_2O_3 nanoclusters on Au(111). The catalytic activity increases with iron oxide coverage initially and then decreases when the coverage is greater than 0.5 ML. Our results suggest that the active sites are located at the iron oxide/gold perimeter. Kinetic measurements suggest that CO oxidation by chemisorbed oxygen at the Fe_2O_3/Au perimeter is likely to be the rate-limiting step. Carbon deposition observed via a post-reaction Auger electron spectra suggests that multiple reaction pathways are involved in CO oxidation over Fe_2O_3/Au(111).

Mechanism-Based Design of Biomimetic Green Oxidation Catalysts

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PROGRAM SCOPE

The goals of this project are to determine the mechanisms of biomimetic catalytic hydrocarbon oxidations with hydrogen peroxide or dioxygen as terminal oxidants, and to identify iron-containing intermediates that are kinetically competent to carry out selective green oxidations. The long-term goal of the project is to apply mechanistic understanding of oxygen and peroxide activation for the development of new, efficient, and selective catalytic systems for multi-electron oxidations.

Dioxygen and hydrogen peroxide are ideal oxidants because they are readily available and environmentally clean, producing water as the only byproduct. These reagents allow for the most efficient, atom-economy approach to oxidative functionalization of organic molecules, thus saving energy in chemical synthesis. In the absence of wastes, there is also no need to use energy for cleaning up the environment. Non-toxic, biocompatible iron complexes will be used as catalysts acting similarly to natural iron-containing oxidative enzymes. Fundamental understanding of multi-electron processes is important for addressing critical issues in converting renewable energy sources into liquid fuels (for example, oxidation of methane into methanol, or catalytic photocleavage of water into hydrogen and oxygen). Additionally, low-temperature kinetic methodology developed in this project will be widely applicable to mechanistic studies of a variety of transition-metal catalyzed homogeneous reactions. Principles uncovered in detailed studies of oxygen and peroxide activation will be also applied to activation of other small molecules, such as carbon dioxide.

FY 2012 HIGHLIGHTS

We successfully characterized the reactivity of high-valent iron oxo species in catalytic olefin epoxidations. Oxygen atom transfer from iron(IV)-oxo intermediates to cyclooctene was observed for the catalysts derived from pyridine azamacrocycles (PyMAC's). However, iron(IV)-oxo species were unable to form epoxides from olefins of phenols from aromatic hydrocarbons in the catalytic systems supported by acyclic aminopyridine ligands. Formally, two-electron oxidations are necessary in these systems. One of the newly designed and synthesized electron-rich complexes gave rise to a novel intermediate that is hypothesized to contain an iron(III)–peroxyacid active species. Chiral ligands for developing enantioselective epoxidations were prepared. Rapid reactions of carbon dioxide fixation with nickel(II)-hydroxy complexes were discovered.

Metal Ion Sites on Oxide Supports as Catalysts for the Water-Gas Shift and Methanol Steam Reforming Reactions

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Funding:	$300,000

PROGRAM SCOPE

The overall goal of this project is to elucidate the role of metal ions anchored on oxide supports and the role of oxide structures in stabilizing the metal ions in their active state for catalyzing reactions of interest to fuel reforming and hydrogen generation. The low-temperature water-gas shift and methanol steam reforming reactions are investigated on atomically dispersed Au and Pt on nanoscale ceria, iron oxide, zirconia, and zinc oxide. The project follows a comprehensive and complementary approach to elucidate the metal-oxide interaction. The creation of stable $M\text{-}O_x$ active sites is a strong function of the size, shape, and composition of the oxide nanoparticles. Single crystal oxides at the nanoscale are prepared and decorated with metal atoms. Such nanocrystals serve as platforms to study how different surfaces bind the deposited metals and to identify potential shape effects for the reactions under investigation. The results are compared to extended single crystal surfaces investigated under vacuum, by co-PIs Sykes and Flynn, bridging the pressure and materials gap between surface science and catalysis.

FY 2012 HIGHLIGHTS

A photodeposition technique was optimized this year to anchor gold atoms on reduced titania sites and demonstrate their comparable activity to gold/ceria for the water-gas shift reaction. Atomic resolution STEM images show the stability of the single gold atoms before and after reaction. In other work, we continue to investigate the addition of alkali as structural stabilizer of metal cations on various supports, and the ensuing high activity of the multinuclear clusters for the reactions of interest. Theoretical work by the Mavrikakis group supports this effort, with work this year focusing on alkali-promoted gold for the water-gas shift reaction. In STM work at Columbia, new findings of the interaction of water with the Fe_3O_4 (111) surface were obtained and reported. Gold atoms on this surface are stably anchored over the uncapped oxygen sites. Along another line, highly selective single atom alloys of Pd/Cu(111) were investigated by STM and TPD as model catalysts with very high selectivity for methanol oxidation to formaldehyde in the presence of co-adsorbed water.

Harnessing the Chemistry of CO_2

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PROGRAM SCOPE

Pollution prevention and waste management continue to be profound challenges for modern society. One potential solution to this problem is the development and utilization of ideal reactions for the production of valuable commodities. In an ideal synthetic reaction, raw materials are converted to the desired product with complete selectivity and without any waste products. Only heat, light, and/or a catalyst are necessary to facilitate the reaction. For example, annulations of unsaturated hydrocarbons with CO_2 could efficiently provide oxygen-containing heterocycles, an important structural motif found in numerous economically important and biologically relevant systems. As added benefits, CO_2 is relatively non-toxic, non-flammable, and abundant and a wide range of unsaturated hydrocarbons are already used in chemical feed stocks on an industrial scale. Although considerable effort has been directed toward the discovery of new and efficient protocols, activation of CO_2 has yet to reach its full potential.

Our research presents several strategies for addressing the challenges of activating CO_2. In addition, our cycloaddition chemistry addresses several fundamental issues pertaining to catalysis as it applies to energy conservation. Our research was highlighted *twice* last year in *Chemical & Engineering News*.

Hydrocarbon Dehydrogenation and Oxidation over Model Metal Oxide Surfaces

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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. Iron oxides and manganese oxides are the current focus of the work. Iron oxides are members of a class of reducible oxide materials important for a variety of applications including catalysis because of the ability of surface cation sites to cycle between different oxidation states (primarily 3+ and 2+). Iron oxide-containing catalysts are active for a wide range of reactions, including CO oxidation, NO_x reduction, water-gas shift, alcohol and hydrocarbon steam reforming, and ethylbenzene dehydrogenation. Chemistry on model (single crystal) iron oxide surfaces is being investigated for insight into the surface properties that control their 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. The chemistry of well-defined hematite (α-Fe_2O_3) and magnetite (Fe_3O_4) surfaces are being examined because they expose iron 3+ and 2+ cations in a variety of surface coordination environments. Similar chemistry is being investigated on manganese oxides (Mn_3O_4 and Mn_2O_3) prepared by the oxidation of the MnO(100) single crystal surface. This extension allows a comparison of the impact of differences in the cation *d*-electron density on the surface chemistry.

FY 2012 HIGHLIGHTS

Work has been completed on the surface diffusion and coupling of methylene on α-Cr_2O_3 surfaces. The preparation and characterization of different manganese oxides on MnO(100) has been investigated spectroscopically and with TPD of a variety of probe molecules. Na deposition has also been examined to stabilize the Mn in a 3+ oxidation state through the formation of $NaMnO_2$ surface layers.

Molecular Understanding of Advanced Catalysis for Hydrodeoxygenation

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PROGRAM SCOPE

Transition metal phosphides have emerged as a new class of catalysts for hydroprocessing, which includes hydrodesulfurization (HDS), hydrodenitrogenation (HDN), and hydrodeoxygenation (HDO). Understanding of the relationship between their physical properties and their catalytic activity is important to develop new improved compositions. This project aims to study this relationship using advanced characterization techniques that can shed light on the nature of the phosphide surfaces during reaction. Use is made of both single crystal models as well as more realistic supported systems for broad understanding. Application is made in both HDS and HDO, with the latter focusing on pyrolysis, a promising thermal route to biomass utilization.

FY 2012 HIGHLIGHTS

The surface structure of Ni2P was determined by STM and LEED. The surface was found to rearrange to form a P-terminated overlayer, which well explained aspects of standard catalysts such as their stability and their partial chemisorptions uptake. A group of transition metal phosphides were evaluated for the hydrodeoxygenation of guaiacol. The activity for HDO of guaiacol follows the order: $Ni_2P > Co_2P > Fe_2P$, WP, MoP. A commercial 5% Pd/Al_2O_3 catalyst was more active than the metal phosphides at lower contact time, but the major product was catechol, which is undesired. The commercial hydrotreating catalyst $CoMoS/Al_2O_3$ deactivated quickly and showed little activity for the HDO of guaiacol at these conditions. These results indicate that transition metal phosphides are promising catalysts for the treatment of bio-derived feedstocks.

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

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PROGRAM SCOPE

Recent increases in the global demand for fossil resources has contributed to volatility in petroleum prices and given rise to price surges. While the increased cost of petroleum most immediately places a stress on the energy sector, the competition for petroleum and other fossil resources influences nearly all sectors that are fed by the chemical industry. Consequently, new technologies that provide useful commodity chemicals at lower cost and with reduced environmental damage are a priority, especially efficient and clean utilization of energy and fossil resources. 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 ability to selectively manipulate C-H moieties of arenes, alkanes and more complex organic molecules would open the door to a wide range of potentially useful synthetic transformations. For example, the 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. The preparation of alkyl and vinyl arenes is practice on a scale of multi-billions of pounds per year, and the products are used for fuels, plastics, soaps and detergents as well as in the pharmaceutical and agricultural arenes. Current routes to alkyl arenes involve the use of acid-catalysts (i.e., Friedel-Crafts catalysts), which have limitations. This project is focused on the development and study of transition metal based catalysts that operate by a mechanism that is different from the Friedel-Crafts catalysts and that offer the opportunity to develop new technologies that improve the preparation of alkyl and vinyl arenes.

FY 2012 HIGHLIGHTS

We have developed new Pt(II) catalysts for olefin hydroarylation and completed mechanistic studies. In one series of complexes, we have shown that the donor ability of ancillary ligands dictates product selectivity (alkyl versus vinyl arene) in a very predictable fashion. In another series of Pt(II) complexes, we have learned how to use ligand sterics to alter the entropy of activation, which can be exploited to enhance catalyst activity at elevated temperatures. We have demonstrated that Fe(II) complexes can activate aromatic C–H bonds at or below room temperature, and these same complexes mediated C–C bond forming reactions. We have shown that deactivation of Ru(II) catalysts is a second order process, which indicates that the deactivation pathway is bimolecular and provides a strategy to increase catalyst longevity.

Observing Carbon-Hydrogen Bond Activation in Chemisorbed Species Using a New Highly Sensitive Optical Method

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

PROGRAM SCOPE

We have discovered a new type of catalytic site called a dual catalyst site. This type of site is located at the perimeter of nanoparticle gold, supported on TiO_2. For the model reaction, CO oxidation, it was found that CO molecules adsorbed on the TiO_2 support, migrated to the perimeter of the Au particles, where oxidation occurred at very low temperatures with a low activation energy of about 0.16 eV. It was found by DFT modeling that the activated step involved the dissociation of an O_2 molecule at the dual Ti-Au site, assisted by the presence of a CO molecule. These sites can be poisoned by excess oxygen.

The special activity of the dual sites was also found for the oxidation of H_2 on Au/TiO_2, where an adsorbed OOH species was postulated theoretically to be a key species.

The decomposition of acetic acid was studied on Au/TiO_2 using infrared spectroscopy. It was found that acetate species on the TiO_2 sites adjacent to Au were selectively oxidized down to the ketenylidene species, Au_2=C=C=O. This minor product may be further oxidized to CO_2. In this case, the removal of C-H bonds from adsorbed acetate occurs on Au sites leading to the novel surface species, Au_2=C=C=O. Current studies underway show that ethylene oxidation proceeds to acetate and then to =C=C=O species.

Separately, we have studied band bending on TiO_2(110) when various adsorbates are added in ultrahigh vacuum. Using the photodesorption reaction of O_2, which is sensitive to band bending, we have witnessed both downward bending from donor adsorbates and upward band bending from acceptor adsorbates. The technique has been extended to Au atoms adsorbed on TiO_2, where downward band bending is observed as a result of slightly positive $Au^{\delta+}$ formation. A massive review concerned with band bending on semiconductors has been published in *Chemical Reviews* and currently enjoys a high rate of recognition. In addition, the sensitivity of absorption IR spectroscopy to changes in the electron density near the bottom of the conduction band of TiO_2 has been used to probe changes in the electronic structure of TiO_2 upon adsorption of CO and H_2.

The interaction of CO and O on TiO_2(110) has been probed using STM and ESDIAD methods and an O..C..O intermediate species has been observed at low temperatures at Ti_{5c} sites.

Structure and Function of Supported Base Catalysts

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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 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 will be 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 and acids, to characterize the nanocrystalline structure of the oxides by Raman spectroscopy, and to evaluate the reactivity of the bifunctional catalysts in steady-state and transient ethanol coupling reactions as well as model aldol condensation reactions.

FY 2012 HIGHLIGHTS

Recently completed isotopic transient analysis of the ethanol coupling reaction to butanol on MgO at 673 K revealed that half of the surface is covered with adsorbed ethanol, identified as ethoxide by DRIFTS, whereas the surface coverage of reactive intermediates leading to butanol was an order of magnitude lower than that of ethoxide. The high coverage of ethoxide and hydroxide inhibited C-C coupling reactions, such as aldol addition reactions, that occur readily on MgO and lead to deactivation.

Novel Palladium Catalysts for the Oxidative Oligomerization of Methane & Carbon Dioxide Reduction

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PROGRAM SCOPE

The long-term goal of this project is to develop novel catalytic transformations that involve less common Pd^{III} and Pd^{I} oxidation states and thus expand further the catalytic reactivity of palladium. The first objective of this project is to develop a novel $Pd^{II}/Pd^{III}/Pd^{IV}$ catalytic cycle for the aerobic oxidative oligomerization of hydrocarbons and various C-C bond formation reactions. The second aim of this project is to investigate the reactivity of Pd^{I} and Pd^{III} systems and develop catalysts for C-C coupling reactions and the activation of small molecules such as CO_2.

The targeted energy-related chemical transformations would allow for a more efficient use of natural gas reserves as an inexpensive energy resource and thus should have a major impact on our society and the environment. In addition, the development of novel catalytic systems for efficient C-C bond formation and the activation of small molecules such as CO_2 will have far-reaching energy-related implications.

FY 2012 HIGHLIGHTS

We have recently reported the first example of aerobic oxidation of a Pd^{II} dimethyl complex that leads to selective elimination of ethane. Detailed mechanistic studies suggest that the aerobic oxidation of the Pd^{II} precursor proceeds through an inner-sphere reduction of O_2 and generation of a Pd^{III} intermediate, while transient formation of Pd^{IV} species is needed for a facile C-C bond formation. Overall, these results show that Pd systems stabilized by judiciously designed ligands can undergo aerobic oxidation, C-C bond formation, and C-H bond activation reactions, and current studies are focused on the development of a catalytic system for the aerobic oxidative coupling of C-H bonds.

We have synthesized a series of mononucleating and dinucleating ligands aimed at stabilizing low-valent Pd centers. In addition, we have recently reported a series of Pd^{II} and Pt^{II} complexes stabilized by a tatradentate N_2S_2-donor ligand that display unique d^8-d^8 interactions between dicationic metal centers. Reactivity studies suggest that these metal-metal interactions can play a role in organometallic reactions and also may be relevant to the activation of small molecules such as CO_2.

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

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PROGRAM SCOPE

Transition metal nanoparticles dispersed across the surfaces of oxide and carbon support materials form the basis for most solid catalysts used for industrial chemical reactions that produce fuels and clean up pollution associated with the generation and use of fuels. They also serve as the best electrocatalysts for fuel cells and photocatalysts for solar energy use. This experimental research program aims to provide the basic understanding needed to develop and improve new catalysts for these important reactions involving nanoparticles of late transition metals supported on oxides or carbon. Specifically, well-defined model catalysts consisting of metal nanoparticles supported on single-crystalline oxide and carbon surfaces are structurally characterized using well-established ultrahigh vacuum surface science techniques and then studied using calorimetry techniques invented here and available nowhere else in the world. The energies of the metal atoms in these particles and the energies of adsorbed intermediates on these particles are measured to determine how these energies depend on the size of the particles and the nature of the oxide or carbon support. The adsorbed intermediates studied here were chosen for their roles in two catalytic reactions (steam reforming of oxygenates and water-gas shift), but are common to many reactions. These energies (which reflect the bonding strengths of these metal nanoparticles to their support and to catalytic intermediates) are correlated with each other and with their catalytic properties (sintering kinetics, elementary-step rates, and net catalytic reaction rates), to clarify how these vary with particle size and the nature of the support surface. This is the key to understanding how and why specific structural properties of catalysts determine their catalytic properties.

FY 2012 HIGHLIGHTS

The heat of adsorption and strength of metal-support interfacial bonding has been measured for Ag atoms in Ag nanoparticles versus particle size on Fe_3O_4(111). Together with our earlier results, we now have a clear picture of how the chemical potential of Ag atoms and the adhesion energy of Ag nanoparticles to oxide surfaces depend on Ag particle size on four different well-defined oxide surfaces: Fe_3O_4(111), CeO_2(111) with two different extents of surface reduction (5 and 10% oxygen vacancies) and MgO(100). Measurements for Cu on CeO_2(111) have begun using a recently constructed calorimeter system that allows study of metals like Cu, Pt, Pd and Au. We reported measurements of the strength of CO bonding to Pd nanoparticles versus particle size for Pd/Fe_3O_4(111). We also wrote a major review of the heats of adsorption of molecules and metals on single crystal oxide surfaces, where we re-analyzed earlier temperature-programmed desorption data to extract more accurate desorption energies using our recently-discovered method for estimating adsorbate entropies and desorption prefactors.

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

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Funding:	$240,000

PROGRAM SCOPE

The rational atomic-scale design of heterogeneous catalysts from fundamental principles has the potential to yield new materials with improved catalytic properties. Using state-of-the-art Density Functional Theory methods, we first elucidate the detailed reaction mechanism of selected catalytic reactions on a number of monometallic surfaces. Trends established through such systematic studies allow for the identification of key reactivity descriptors, which are then utilized for designing bimetallic and ternary alloy catalysts with improved catalytic properties. Because the composition and architecture of catalytic nanoparticles predicted by theory play an important role in determining their catalytic properties, we develop and implement sophisticated nano-synthesis methods for synthesizing the theoretically-predicted optimal nanostructures. Having synthesized these new catalysts, we then characterize and evaluate them experimentally.

In particular, we are interested in identifying and synthesizing new catalysts for: (1) nitric oxide (NO) reduction by H_2, (2) CO-tolerant electro-oxidation, and (3) ammonia (NH_3) and dimethyl ether (DME) electro-oxidation. Our research is driven by the quantum mechanical atomic-scale design of the active site and is facilitated by the controlled synthesis of the theoretically-identified sites using inorganic synthesis techniques capable of yielding metal and alloy nanoparticles with controlled shape and size, thereby taking advantage of reactions' structure sensitivity.

The proposed fundamental research, using a combination of theory and experiments, should have a significant impact on designing catalysts at the nanoscale. These new catalysts could greatly facilitate the reduction of nitric oxide to dinitrogen, the bypassing of CO poisoning of anodes in fuel cells, and the usage of ammonia and dimethyl ether as fuel in direct, low temperature, fuel cells—the former being relevant to environmental pollution remediation, and the latter two to increasing energy efficiency of power generation in portable applications.

FY 2012 HIGHLIGHTS

We have analyzed the reaction mechanism and structure sensitivity of NO reduction by H_2 and of DME and NH_3 electro-oxidation on several monometallic surfaces, both in terms of thermochemistry and activation energy barriers of the elementary steps involved. This provides the necessary groundwork to proceed towards the development of a comprehensive micorkinetic model, which eventually will lead to the development of volcano plots (activity versus key reactivity descriptors), allowing for the identification and synthesis of promising alloy catalysts. In parallel, we have identified from theory a number of trimetallic alloy surfaces, promising for their improved CO-tolerance.

Copper-Catalyzed Aerobic Oxidation of Arenes and Alcohols

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PROGRAM SCOPE

This project seeks to address 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 research specifically focuses 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. In the proposed research, we will expand these efforts, targeting 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 2012 HIGHLIGHTS

We have addressed two principal objectives: (1) investigation of the mechanism of Cu-mediated activation of arene C–H bonds, in particular, probing the factors that contribute to single-electron-transfer and organometallic C–H activation pathways, and (2) elucidation of the mechanism of copper(I)/TEMPO-catalyzed aerobic oxidation of primary alcohols (TEMPO = 2,2,6,6-tetramethyl-piperidin-1-yl)-*N*-oxyl). In the first area, we have identified an arene substrate that undergoes Cu^{II}-mediated oxidative functionalization of two different C–H bonds in the molecule. Systematic studies of these reactions reveal that the two different products arise from two different mechanistic pathways, one initiated by single electron transfer from the arene to Cu^{II} and the other initiated by Cu^{II}-mediated organometallic C–H activation. In the second area, we have investigated a highly active catalyst system for chemoselective oxidation of primary alcohols to aldehydes, which consists of a $(bpy)Cu^{I}X$ complex (X = non-coordinating anion) in combination with TEMPO as a redox active organic cocatalyst. This catalyst system represents one of the most effective methods reported to date, and it is effective even with aliphatic alcohols, which are often poorly reactive and/or susceptible to overoxidation. Mechanistic studies of these reactions highlight the cooperative redox chemistry associated with the Cu and TEMPO cocatalysts, and reveal key differences between reactions of activated alcohols, such as benzylic and allylic alcohols, relative to unactivated aliphatic alcohols.

Fundamental Studies of the Reforming of Oxygenated Compounds over Supported Metal Catalysts

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PROGRAM SCOPE

The goal of this project is to elucidate the fundamental surface chemistry involved in the catalytic conversion of renewable biomass resources to produce liquid fuels and chemicals. This work will have potential impact to the Department of Energy by providing a fundamental basis for catalytic strategies in the utilization of both cellulose and hemi-cellulose. During the past year, our group has investigated catalytic processes for the conversion of cellulose-derived levulinic acid to gamma-valerolactone (GVL). Because levulinic acid and formic acid are typically produced from biomass in aqueous solutions of sulfuric acid, we studied a reactive extraction step in which levulinic and formic acids are converted to hydrophobic esters that spontaneously separate from the aqueous phase. Based on this new extraction step, we then initiated fundamental studies to elucidate the performance of supported metal catalysts for the conversion of these hydrophobic esters (i.e., butyl levulinate and butyl formate) to fuels and chemicals.

FY 2012 HIGHLIGHTS

We found it is possible to convert butyl levulinate to GVL over a Ru/C catalyst; however, the Ru/C catalyst leads to the undesirable dehydration of formic acid to CO and H_2O, followed by methanation of CO. Importantly, we showed that it is synergistic to combine the catalytic properties of Pd/C and Ru/C in a dual-catalyst-bed reactor to achieve in situ hydrogen generation from formic acid on Pd/C alongside GVL production on Ru/C. To elucidate the underlying kinetics of this ester system, we explored the liquid-phase reactivity of formic acid and butyl formate over Pd/C. Studies at different space velocities were carried out to elucidate the individual kinetic contributions of the primary decomposition pathways, secondary water gas shift (WGS) reaction, and homogeneous chemistry in solution. We showed that formic acid reacts primarily via decarboxylation (to CO_2/H_2), whereas butyl formate primarily reacts via decarbonylation (to CO/butanol). When water is present, the formate ester undergoes hydrolysis, which increases the selectivity towards CO_2 and H_2.

In recent work, we have studied the liquid-phase hydrogenation of furfural (produced from hemi-cellulose) to furfuryl alcohol (an intermediate that can be converted to levulinic acid). We have shown that copper based catalysts are selective for FuOH production; however, these catalysts undergo leaching of copper in the liquid phase. Importantly, we have found that a PtSn/C catalyst resulted in high furfuryl alcohol selectivity (98%), with a furfuryl alcohol production rate that was an order of magnitude higher compared to the other bimetallic catalysts (i.e., Ru:Sn and Pd:Sn). Moreover, even though the PtSnC catalyst deactivated with time-on-stream, it could be regenerated completely through calcination in air, showing that coking was the main reason for deactivation.

Metal-Metal Bonded Reaction Intermediates in C-H Functionalization

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PROGRAM SCOPE

The goal of this research is to define the fundamental coordination chemistry and mechanisms of C–H functionalization by metal-metal bonded compounds of Ru and Rh of the general formula $M_2(\text{ligand})_4$, where M = Ru or Rh and ligand = a monoanionic, bridging ligand. We have explored two distinct research directions: (1) inquiry into the mechanism of dirhodium-catalyzed carbene and nitrene transfer reactions, and (2) exploration of C–H amination by well-defined diruthenium nitride compounds.

FY 2012 HIGHLIGHTS

Major advances in both research directions have been made. In area (1), we have brought to bear our new-found insights in the mechanistic understanding of Rh_2(II,II)-catalyzed C–H amination to catalyst design. We have reported novel Rh_2 catalysts bearing redox non-innocent ligands, marking the first time such ligands have been used with metal-metal bonded compounds. We have also synthesized a new stable mixed-valence Rh_2(II,III) catalyst for C–H amination that allows high turnover numbers to be achieved in intramolecular reactions. We are currently finishing our study of the spectroscopic characterization of the first observable Rh_2 carbene complex and its reactivity.

In area (2), we have published a major computational study of C–H amination by bimetallic nitrido compounds to assess the role of the metal-metal bond in affecting the ground and transition state energies for aryl C–H amination via electrophilic aromatic substitution as well as the prospect of forming the nitrido compounds from N_2. To allow for intermolecular nitrido reactions, we have designed new sterically unencumbered nitrido compounds, which perform N atom transfer and can be regenerated in a synthetic cycle. We have also published a 'Perspective' article in *Dalton Transactions* outlining the developing relationship between electronic structure and C–H functionalization reactivity in both nitrido systems and catalytic dirhodium systems.

Molecular-Level Design of Heterogeneous Chiral Catalysts

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Funding:	$650,000

PROGRAM SCOPE

Chiral catalysts are capable of producing enantiomerically pure chiral compounds from prochiral reagents. This enantioselectivity is arguably the most subtle form of selectivity in heterogeneous catalytic processes because it is induced by enantiospecific differences in reaction energetics that are of the order of a few kJ/mole. As such, a fundamental understanding of the origins of enantioselectivity can have broad impact on our understanding of catalytic selectivity in general. The program has been a collaborative effort to gain a fundamental understanding of the origins of enantioselectivity on the three types of chiral surfaces: naturally chiral metal single crystal surfaces, metal surfaces modified with a chiral template of adsorbates, and metal surfaces with one-to-one chiral modifiers. The naturally chiral single crystal surfaces are those that have atomic structures lacking mirror symmetry and, therefore, exist in enantiomorphous pairs. Chirally templated surfaces are those with adsorbate overlayers having long-range order but lacking mirror plane symmetry. The one-to-one modifiers are adsorbed ligands that are themselves chiral and, therefore, impart chirality to the surface. The program brings together a wide array of experimental methods and computational tools to enable the measurement and modeling of enantiospecific interactions between chiral probe molecules and these three types of chiral surfaces. While there are many groups worldwide that have observed chiral structures on surfaces using various methods for surface structure determination, our collaboration has made the greatest single collective contribution to the much more challenging problem of detecting and studying enantiospecific surface chemistry on these chiral surfaces.

FY 2012 HIGHLIGHTS

Aspartic acid has been identified as a species that will undergo reaction on chiral Cu(3,1,17)$^{R\&S}$ surface by an explosive mechanism that leads to extremely high enantiospecificity. Because it is an amino acid, L-Asp can be obtained in many different isotopomeric forms that are enabling us to unravel the details of the surface reaction mechanism. The enantiospecific templating of Pd(111) surfaces by amino acids has been shown to require the formation of amino acid tetramers on the surface. The immobilization of cinchona alkaloids on porous silica supports by flexible tethers has been shown to impart enantioselectivity to catalytic reactions on these surfaces. The flexibility of the tether is an important parameter in determining enantioselectivity.

Atomic Resolution Imaging and Quantification of Chemical Functionality of Surfaces

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Funding:	$140,000

PROGRAM SCOPE

The work carried out in this project comprises an atomic-scale study of the local chemical interactions that govern the catalytic properties of model catalysts that are of interest to DOE. This goal is achieved through three-dimensional atomic force microscopy (3D-AFM), a new measurement mode that allows the mapping of the complete surface force and energy fields with picometer resolution in space (x, y, and z) and piconewton/millielectronvolts in force/energy. In combination with the simultaneous recording of tunneling current (3D-AFM/STM), chemically well-defined tips, chemical interactions can be precisely quantified and assigned to exact positions within the lattice. To further improve on imaging robustness and to expand the information that can be obtained from the measurements, we are pursuing, as an integral part of this proposal, several routes for instrumental and methodological upgrades.

FY 2012 HIGHLIGHTS

During the FY 2012 reporting period, we had three main activities. First, we had a deeper look at the interplay between tip apex chemistry and the imaging of the oxygen/copper (100) Cu_3O_2 surface phase. Second, we worked on the 3D imaging of the rutile TiO_2 surface, the most widely employed photocatalyst. Third, we started preliminary work on SiO_2 films on Pd(100). The work on the analysis of the oxygen/copper (100) Cu_3O_2 surface phase imaging was particularly detailed, and involved the complete clarification of how tip chemistry, bias voltage, tip-sample distance, and the simultaneous recording of STM and AFM signals affect the collected data in terms of image contrasts, image artifacts, and achievable information. As a result, we could show strategies for tuning the species-specific image contrasts in both STM and AFM, thereby making significant headway with regards to establishing new approaches that ultimately lead to a complete understanding of structural, chemical, and electronic surface properties. On TiO_2, we also demonstrated chemical sensitive, three-dimensional imaging that depended on tip apex chemistry, but allowed again a de-coupling of chemical and electronic interactions. Finally, we were able to resolve the complete atomic structure of an amorphous bilayer of SiO_2 grown on Pd(100) using STM. Changing the bias voltage during imaging then allowed us to visualize bonding abnormalities caused by the irregular structure of the material.

Bifunctional Ligands for Enhanced Selectivity in Organometallic Catalysis

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Funding:	$150,000

PROGRAM SCOPE

The supply of precious metals is not keeping up with demand, and more sustainable homogeneous catalysts than our usual Ir catalysts will soon be needed. We are therefore looking for strategies for endowing 1st row d metals or Mo and W with comparable activity to that we now see for Pt metals. With the sharply increasing prices of these metals, we expect a very big cost advantage in moving from our usual Ir ($16,800/lb) to Co ($40/lb). The iridium price has been strongly affected by its increasing use in flat screen displays. Chirik and Wieghardt have highlighted redox active ligands in the context of the 1st row metals, but here we explore bifunctional ligands with proton transfer ability. Moving to them may require adopting different catalytic mechanisms than common for the precious metals, however. Instead of oxidative addition/reductive elimination (OA/RE) cycles, we propose H+/H- transfer.

FY 2012 HIGHLIGHTS

Our DOE catalysis papers continue to be very highly cited—eight such papers were newly published in FY 2012, one of which has already been cited 20 times. The most interesting new and unpublished development is a metal-free catalytic hydrosilylation procedure, metal-free operation obviously being the most sustainable possible situation with reference to metal usage.

In a spin-off from an EFRC discovery, a nickel pincer complex carries out reactions of interest to the DOE catalysis program that are far beyond the scope of the EFRC, and we can thus transfer the new catalysts to the DOE catalysis program when the anticipated new DOE catalysis coworker joins the group. In particular, electrocatalytic reduction of polar C=X bonds and even of CO_2 look as if they will be possible.

Finishing up work from the prior grant period, we have discovered a tandem hydrogenation reductive alkylation procedure in which N-heterocycles are reduced by H_2 and alkylated by RCHO. This so far only works with Ir, however, and not with any of our cheap metal catalysts.

In a spin-off from DOE catalysis work, some of the Co and Ni catalysts we have developed have proved useful for oxidation of lignin model compounds in a collaboration with the Anastas green chemistry group.

Fabrication of Epitaxial Cobalt Oxide Thin Films for the Structure and Reactivity Study in Catalysis

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Funding:	$155,000

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 begun 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 2012 HIGHLIGHTS

We have successfully grown epitaxial cobalt oxide thin films up to 2 ML thick on Au(111). At 0.2 ML, the films grow as single monolayer high, rocksalt-structured CoO(111) islands with {110} oriented step edges; the lattice mismatch between CoO and Au results in a moiré patterned surface structure. Above a critical film thickness of 0.4 ML, the same growth conditions produce solely spinel-type Co_3O_4(111) islands. The lattice match between the spinel and Au(111) is nearly perfect, and so the island surfaces lack the moiré pattern seen for CoO. Instead, the islands adopt a characteristic tri-star pattern due to grain boundaries embedded in the islands. Above the critical thickness, the surface structure and morphology of the films can be modulated by varying the temperature and oxygen chemical potential both during growth and in post-growth treatments. As a result, three-dimensional islands of both CoO and Co_3O_4 could be produced. At 1 ML, the CoO and Co_3O_4 islands adopt similar distorted hexagonal shapes; above 2 ML, multilayer Co_3O_4 islands become triangularly shaped, suggesting a higher step energy anisotropy for multi-atom steps versus single height steps.

We have shown that oxidation and reduction leads to reversible cycling of the bulk and surface structure of the Co oxide islands. When hexagonal CoO islands are oxidized, the characteristic moiré pattern is replaced by the Co_3O_4 tri-star pattern; reduction causes the surface to revert to the moiré pattern. We show that this reversible cycle is due to preferential oxidation of the CoO islands from three crystallographically equivalent island edges which leads to grain boundaries when the reaction fronts converge. The results demonstrate structure sensitivity of cobalt oxide reactivity; we are pursuing understanding the role this structure sensitivity plays in the intriguing catalytic activity of Co oxides.

Structured Carbon Supports for Aqueous Phase Reforming and Fuel Cell Catalysts

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Funding:	$160,000

PROGRAM SCOPE

The goal of this project is to design, characterize, and demonstrate utility of an oxide/multi-walled carbon nanotube (MWCNT) composite catalyst support for aqueous phase metal hydrogenation and acid catalyzed biomass reactions. The prototypical platform that we have developed is ZrO_2/MWCNT using Pt as the exemplary metal for hydrogenation (and aqueous phase reforming) and sulfated ZrO_2 (S-ZrO_2) as the exemplary acid for hydrolysis and/or transesterification. Multiple characterization methods have been used, including physical adsorption, chemisorption, catalytic probe reactions, point of zero charge, TEM, XRD, and FTIR, for characterization. Particular emphasis was placed on synchrotron x-ray absorption spectroscopy to characterize the interfaces between ZrO_2 and MWCNT (oxygen bonding between Zr and C) and between the sulfate species and ZrO_2.

FY 2012 HIGHLIGHTS

The nature of the sulfated ZrO_2 interface has been analyzed by near edge x-ray absorption fine structure (NEXAFS) at the O K-edge, Zr L-edge, and S K-edge. This technique allows us to probe the valence molecular orbitals between O, Zr, and S to identify the Zr d (e_g) orbitals as the primary bonding species with S, demonstrate charge transfer from Zr to S (increasing the Brønsted acidity on S), and provide a method to follow the reaction of the sulfate ion with the ZrO_2 surface upon thermal treatment.

To synthesize hydrothermally stable nano particles of ZrO_2 on MWCNT, the MWCNT first must be functionalized. This usually involves some form of oxidation to create oxygen containing groups (OCG) bonded to the MWCNT, to which the Zr precursor may be grafted. However, a second approach is to thermally decompose the OCG and thus create oxygen free defects. We have demonstrated that these defects can also be used to anchor ZrO_2. Because all of the excess OCG (not involved in bonding of the Zr precursor) has been removed, the MWCNT at the ZrO_2 provides a more hydrophobic environment for the ZrO_2 nano particles and is therefore less susceptible to hydrolysis under reaction conditions. In the next period, we plan to compare the hydrothermal stability of nano particles of Pt and Ru (a more oxophilic metal) when anchored to defects in MWCNT (created by thermal decomposition of OCG) and to synthesize and characterize tungstated ZrO_2/MWCNT and compare its catalytic acidity with that of sulfated ZrO_2/MWCNT.

DOE National Laboratories

Homogeneous and Interfacial Catalysis in 3-D Controlled Environments

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Funding:	$1,320,000

PROGRAM SCOPE

This collaborative research effort involves developing and characterizing multifunctionalized mesoporous materials that integrate the selectivity of novel homogeneous catalysts with the thermal/chemical stability and separability of heterogeneous catalysts. The control of surface properties is achieved by multifunctionalization, where some of the anchored groups serve as catalysts, while others modify the selectivity or activity of the system. The catalytic activity of these single-site heterogeneous catalysts is being examined for several classes of chemical reactions, including enantioselective hydrogenation, hydroamination, bond activation, and oxidation. The 3-D catalytic materials are studied using various chemical, physical, and theoretical methods, highlighted by new solid-state nuclear magnetic resonance (SSNMR) techniques developed within this project and computational modeling based on non-equilibrium statistical mechanics.

Developing catalytic systems that can coherently unite the best features of the homogeneous and heterogeneous areas of catalysis is a key interest of the DOE. By controlling the structure, reactivity, and morphology of a mesoporous solid support and its interaction with active sites, these studies provide truly unique opportunities for the design of a new generation of highly efficient and selective catalysts. This research also provides fundamental knowledge about catalysis by deconvoluting the key factors that affect selectivity, reactivity, and kinetics.

FY 2012 HIGHLIGHTS

Scientists used innovative synthetic strategies and new SSNMR methods to develop an improved catalyst for a carbon-carbon bond forming reaction routinely used in chemical manufacturing and biofuel production. This heterogeneous catalyst is significantly more active than homogeneous catalysts, contrary to expectations. SSNMR showed that mesoporous support brings the reactants and catalytic groups together, resulting in enhanced, cooperative activity not possible with the untethered catalyst. Additionally, scientists helped solve an 80-year-old puzzle about a widely used chemical process. The Fenton reaction involves iron and hydrogen peroxide and is used to treat wastewater worldwide. The exact nature of the intermediate, a radical or non-radical iron species, has been debated for decades with data to support both types. Researchers proved that both intermediates can be involved; it just depends on the pH. In an acidic environment, the intermediate is an hydroxyl radical; whereas at near neutral pH, the intermediate is Fe(IV). Researchers also showed that light, combined with a novel rhodium catalyst, enables greener production of chemical feedstocks from biorenewables. A key challenge in the utilization of biomass for fuels and fine chemical applications is the control of oxygen and nitrogen-containing functional groups. Unfortunately, current routes also generate unwanted by-products. This rhodium catalyst converts primary alcohols into hydrocarbons at room temperature through tandem catalytic reactions. One reaction removes hydrogen from the alcohol producing valuable H_2, while the other removes carbon and oxygen and produces carbon monoxide and a hydrocarbon.

Institute for Catalysis in Energy Processes

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Funding:	$900,000

PROGRAM SCOPE

The Institute for Catalysis in Energy Processes (ICEP) is a collaboration between Argonne National Laboratory and Northwestern University directed toward understanding and advancing the catalytic transformation of unreactive molecules. The research is focused on two efforts: the catalytic oxidation of small alkanes (e.g., methane and ethane) and the photocatalytic reduction of carbon oxides (e.g., CO_2). The Argonne portion of ICEP comprises activities in (1) synthesis and molecular characterization of supported oxide catalysts used for alkane oxidation and (2) understanding photocatalytic reactions catalyzed by TiO_2.

New synthesis methods for the formation of catalytic oxide monolayers have been explored using atomic layer deposition and organometallic grafting. Exquisite control has been accomplished of surface oxide species that are highly active for alkane activation and in forms that are amenable to catalytic, spectroscopic, and structural investigation. Catalytic studies are performed in fixed-bed flow reactors. Spectroscopic characterization is by advanced resonance Raman spectroscopy and associated computational studies. Structural studies use the Advanced Photon Source at Argonne for x-ray absorption and x-ray standing wave measurements.

Experimental investigations of TiO_2-catalyzed photoreduction of CO_2 using water have utilized powerful electron paramagnetic resonance (EPR) at Argonne to elucidate the reaction mechanism. In a computational study that is linked to the EPR experiments, the key reaction steps can be identified and analyzed. This work lays the foundation for better understanding of photocatalysis and the design of more effective processes.

FY 2012 HIGHLIGHTS

Surface vanadium oxide species supported on alumina and titania have been synthesized that are highly active for alkane activation. Tridentate, bidentate, and monodentate vanadia species have been detected. The bidentate species were shown to have the highest activity for hydrogen activation. On titania supports, the vanadia species are observed to form the same structures during oxidation and reduction with both hydrogen and alkanes.

In photocatalysis by titanium dioxide, direct evidence has been obtained for the role of water in enhancing the population of surface electron-hole pairs, the species responsible for the desired chemistry. EPR has also detected radical intermediates in the reaction path to the final products of methane and methanol. In a computational study, the key reaction steps have been identified and analyzed.

Metalated Porous Organic Polymers as Advanced Catalysts for Hydrocarbon Transformations

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Funding:	$400,000

PROGRAM SCOPE

The key to catalytic functionalization of challenging substrates, such as CH_4 and simple alkanes, is the ability to simultaneously control the reaction geometry, reagent flow, and orientation in three dimensions. Designing selective catalysts requires a fundamental understanding of how to synthesize active site configurations that optimize these properties with precise control over the geometry of all the components. We will exploit the modular, flexible, and tailorable nature of covalent porous organic polymers (POPs) to develop well-defined single site catalysts from early and earth abundant transition metals (e.g., tantalum and iron, respectively) inside these reactivity-defining microenvironments. As part of this effort we will (1) explore the reversible catalytic framework-building reactions, olefin metathesis and alkyne metathesis, to understand the parameters required to afford robust crystalline POPs containing specific metal binding moieties; (2) develop general strategies for metalation inside these POPs and elucidate the factors controlling metal speciation, particularly the low-coordinate metal hydride and hydrocarbyl species key to alkane metathesis; and (3) alter the selectivity in catalytic hydrocarbon reactions by exploiting the pore size of the POPs. With these catalytic materials, we will probe the C-H and c-c bond breaking and making steps required for direct natural gas conversion to liquids.

FY 2012 HIGHLIGHTS

A catechol-functionalized porous organic polymer (POP) has been successfully metallated with a Schrock-type Ta^V alkylidene and remains thermally and structurally robust. The resulting POP-supported (catecholato)Ta^V alkyl sites remain accessible to small molecules and can undergo reactions to yield stable, monomeric complexes that are quite different to those observed with the homogeneous analogs. Using a combination of reactivity studies, high-resolution solid-state NMR spectroscopy, and x-ray absorption spectroscopy, we are able to precisely determine the functionality and coordination environment of the active (catecholato)Ta^V alkyl site and its products in reactions with Brønsted acids.

Structure/Composition/Function Relationship in Supported Nanoscale Catalysts for Hydrogen

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Funding:	$730,000

PROGRAM SCOPE

The objective of the research is a fundamental understanding of composition/structure/function relationships in supported, heterogeneous catalysts for reactions that produce hydrogen from hydrogen-rich molecules. This project examines the role of particle composition, size, and structure and the effect of supports and promoters on adsorptive and catalytic properties. The catalysts are supported metal and alloy nanoparticles and clusters with an emphasis on supported catalytic clusters in the size range <1 nm down to single atoms. The proposed research integrates efforts in: (1) synthesis and stabilization of uniform, supported clusters and oxide promoters; (2) characterization of cluster size, atomic structure, stability, and electronic structure during synthesis, pretreatment, and catalytic reaction; (3) investigation of catalytic and chemical events on the clusters; and (4) computational quantum chemical modeling to understand and predict experimental results.

FY 2012 HIGHLIGHTS

A major outcome from the research has been the development of atomic layer deposition (ALD) as a method for catalyst synthesis and stabilization. Oxide supports, late transition metals and alloys on these supports, and stabilizing oxide overcoats on top of the metals have all been synthesized by ALD. The oxide overcoats have been shown to prevent both particle sintering and coke formation that are responsible for deactivation of supported metal catalysts during ethane dehydrogenation. Spectroscopic studies demonstrate that the overcoats function by blocking and stabilizing under-coordinated metal atoms at edge and corner sites on the particle surface. These results suggest a number of strategies for improving the performance of heterogeneous catalysts operating under high temperature, hydrocarbon environments.

Catalysis on the Nanoscale: Preparation, Characterization, and Reactivity of Metal-Based Nanostructures

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Funding:	$550,000

PROGRAM SCOPE

The general goals of this program are to identify and characterize the catalytically active sites of supported nanocatalysts and investigate how these are influenced by variations in particle size, morphology, and support. Current efforts are focused on model catalysts composed of supported transition metal carbide, oxide and sulfide nanoclusters for desulfurization, hydrogen production, oxygenate synthesis, and electrooxidation. Unique experimental capabilities include mass-selected cluster deposition for preparing monodisperse cluster distributions, a new instrument with capabilities for UHV characterization and electrochemical activity measurements, and a new STM with high temperature and near ambient pressure capabilities. Theoretical investigations using DFT and kinetic modeling are an integral part of this program and are used to explore the role of light atoms (C, S, P) or dopant metals in modifying the activity of metal catalysts, the influence of cluster-support interactions on reactivity, and the identification of key intermediates and reaction steps in complex surface reactions. The experimental and theoretical characterization of well-defined model catalyst surfaces provides a basis for understanding the unique chemical activity of supported nanoclusters which can be used for the development and optimization of catalyst materials for energy production and utilization.

FY 2012 HIGHLIGHTS

Using a newly developed instrument with combined UHV surface characterization and electrochemical testing capabilities, we have discovered the mechanism for a strong size-dependence of SnO_x promoted Pt electrodes for the electrooxidation of methanol/ethanol. In particular, the presence of partially reduced Sn (II) species in small SnO_x nanoparticles ($\leq$ 3 nm) enhances the oxidative removal of surface CO, which normally poisons the Pt electrode surface. DFT calculations showed that the Sn-OH bond is weaker on small SnO_x particles supported on Pt, thereby enhancing their ability to oxidize CO.

The introduction of O-atoms by ion sputtering was shown to transform the relatively inert Au (100) surface to a highly reactive surface which can act as a highly selective, low temperature catalyst for oxidation reactions. Using STM imaging, photoemission, and thermal desorption techniques along with DFT calculations, we were able to show that the highly reactive surface is a result of an increase in the number of under coordinated Au atoms and lifting of the surface reconstruction.

Theoretical studies were able determine the growth mechanisms, atomic structures, and electrochemical activities of core (Ru,Pd)-shell (Pt) nanoparticles for the oxygen reduction reaction and established more realistic models to describe the unique catalytic behavior of TiO_2-supported sub-nanometer Pd clusters under CO oxidation conditions.

Catalysis: Structure and Reactivity

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Funding:	$1,143,000

PROGRAM SCOPE

The goal of this program is to provide an improved understanding of chemical catalysis by elucidating details of the fundamental properties of molecules, surfaces, and their reactions that are critical to catalysis and energy conversion. Reactivity-structure correlations explored and unraveled by utilization of synchrotron radiation are a key aspect of these studies. 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. In the former, emphasis is placed on understanding basic principles of surface reactivity and its control by surface modification, on identification of active sites and full characterization of their electronic and structural properties. X-ray photoemission and absorption spectroscopies at beamline U7A of the National Synchrotron Light Source are essential to this work. In the latter systems, in-situ time-resolved studies of the formation and transformations of powder catalysts under catalytic reaction conditions are carried out using our x-ray diffraction facility at beamline X7B and facilities for x-ray absorption spectroscopy at beamlines X18A,B and X19A. Quantum-chemical calculations based on density-functional theory are performed to help in the interpretation of experimental results and to study basic aspects of catalytic reactions.

FY 2012 HIGHLIGHTS

(1) We discovered the special structural and chemical properties of RuO_x nanoparticles in contact with TiO_2 (110). On this titania surface, the RuOx forms nanowires that are quite reactive towards O_2 and water, making RuOx/TiO2 (110) an excellent substrate for the oxidation of CO. (2) In a series of experiments, it was established that mixed-metal oxides can play an important role in the synthesis of alcohols through the hydrogenation of CO_2/CO and in the reforming of ethanol. New catalysts have been developed that combine non-expansive metals (Cu, Ni, W) with a CeO_2 matrix. (3) We are continuing work in a new family of Au-TiC and Cu-TiC catalysts which show excellent activity for the synthesis of methanol via CO_2 hydrogenation. (4) The Catalysis Group has been actively involved in the design of three beamlines for catalysts characterization at the NSLS-II.

Mechanisms for Water Gas Shift Reaction

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Funding:	$650,000

PROGRAM SCOPE

The water-gas shift reaction (WGS: $CO + H_2O \rightarrow H_2 + CO_2$) is a critical process in providing pure hydrogen for fuel cells and other applications. Improved air-tolerant, cost-effective water-gas shift (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 2012 HIGHLIGHTS

(1) We discovered a new type of metal-support interaction that can be quite useful for the rational design of highly active water-gas shift catalysts. (2) Studies carried out using inverse oxide/metal catalysts showed the important role played by the oxide phase in the WGS reaction. This led to a shift of paradigm for the design of WGS catalysts: the optimization of the properties of the oxide phase is as important as the optimization of the metal phase. (3) Highly active powder catalysts that combine Au or Pt and CeO_2 nanoparticles on a titania substrate were prepared and fully characterized. (4) We participated in the development of new tools and techniques for the in-situ characterization of water-gas shift catalysts, helping in the design of a new instrument that will combine XAFS with infrared or Raman spectroscopy. This new instrumentation will allow us to perform unique mechanistic studies.

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

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Funding:	$720,000

PROGRAM SCOPE

The scope of this program is to study basic problems of electrocatalysis of fuel cell reactions while focusing on platinum monolayer electrocatalysts for the O_2 reduction reaction, and ternary and bimetallic electrocatalysts for ethanol and methanol oxidation. Studies using well-defined single crystal surfaces, as well as well-defined nanoparticles with ordered structure, will be carried out to gain understanding of the atomic-scale phenomena involved in the interactions of Pt monolayers with supporting surfaces. By kinetic modeling and computational methods, we will obtain deeper insight into the kinetics of the O_2 reduction reaction and alcohol oxidation, the role of proton transfer, and the bonding of O_2, O, and OH, and reactants and intermediates in alcohol oxidation. The results will provide a basis for synthesizing the electrocatalysts for O_2 reduction having high activity, high stability and an ultra-low Pt content, and high-activity electrocatalysts for oxidation of organic molecules. We demonstrated that the electrochemical deposition of Pd nanowires is possible on functionalized carbon nanoparticles. The mechanism of 1D growth of Pd on carbon has been proposed.

The new mechanism facilitating the stability of core-shell nanoparticles, involving shell protected by the core, will be further explored, as well as hollow nanoparticles catalysts and the stabilization of cores by alloying or by placing subsurface metal monolayers—the second generation of core-shell nanoparticles. We will expand studies of ternary catalysts for ethanol oxidation and, particularly, new discovery of pronounced increase of catalytic activity of Pt for ethanol and methanol oxidation induced by tensile strain caused by support. The success of our work will greatly contribute to resolving the major problems in existing fuel cell technology, which are related to the electrocatalysts costs and performance.

FY 2012 HIGHLIGHTS

Electrocatalytic activity of Pt for oxidation of alcohols can be increased through support-induced lateral strain in Pt monolayers on metal substrates. The strain-activity correlation was established for five Pt/support couples. Methanol and ethanol oxidation for Pt_{ML}/Au (111) exhibit a factor of 7 and 4 activity increase relative to Pt (111), respectively.

We demonstrated an electrochemical deposition of Pd nanowires on functionalized carbon nanoparticles. The one-dimensional growth of Pd is ascribed to the hydrogen-underpotential-deposition-mediated layer-by-layer deposition of Pd. The surface structure of deposited nanowires is composed predominantly of the {111}-oriented facets that facilitate the enhanced oxygen reduction and high stability of these electrocatalysts.

Ultrafast and Chemically-Specific Microscopy for Atomic-Scale Imaging of Nano-Photocatalysis

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Students:	2 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$420,000

PROGRAM SCOPE

This program's objective is the ultrahigh-resolution spatiotemporal investigation of heterogeneous photocatalysis. We are investigating both photon- and electron-induced surface physics that drive photocatalytic surface chemistry. Our main initial focus has been on the development of ultrafast-laser-excited scanning tunneling microscopy methods to achieve simultaneous subnanometer and subpicosecond resolution of surface electronic excitation.

Heterogeneous photocatalysis involves the transfer of charge and energy from the photoexcited catalyst to adsorbate molecules. Reaction efficiency is governed by a series of factors whose detailed interrogation poses a formidable experimental challenge. These factors include excitation and relaxation of hot charge carriers (electrons or holes) with lifetimes that may be surface-site dependent; hot-carrier capture into adsorbate affinity levels with energies that may also be surface-site dependent; and energy transfer to non-electronic degrees of freedom. This program addresses the long-standing challenge of characterizing these factors, and the resultant chemical transformations, at the single-molecule level and with subpicosecond time resolution by: mapping the dynamics of nonequilibrium hot-carrier populations and the chemical reactions they drive, identifying chemical species on photocatalysts, and investigating the reaction pathways and mechanisms of non-thermal, electron-mediated chemistry. Our effort aims to understand photoinduced processes on nanostructured model photocatalyst surfaces at a level of detail that can make important contributions to the rational design of next-generation materials for solar photocatalysis.

FY 2012 HIGHLIGHTS

We have established the importance of eliminating pump–probe optical interference to mitigating undesired thermal modulation of the STM tip length. We have achieved ultrahigh spatial resolution of ultrafast photoexcitation of nanometer-scale particles. Measurements intended to extend this success to semiconductor surfaces (InAs, InAs nanowires) have shown decay times that depend on excitation wavelength with good signal-to-noise ratios. However, efforts to spatially resolve these transients have yet to succeed. We have also demonstrated that electronic excitation of surface oxygen vacancies on TiO_2 can induce a transient mobility that points to a formation pathway for highly reactive vacancy pairs. Statistical analysis of the pairwise separation of these vacancies has provided a basis for quantifying the elastic interaction between vacancies—an interaction key to understanding their distribution as reactive sites on TiO_2 surfaces.

Future work will spatially-resolve the photoinduced chemistry of model electron acceptor compounds (e.g., halogenated hydrocarbons) and water on metal-nanoparticle arrays and graphene layers supported on semiconductor surfaces.

Nanoscience & Nanoparticles for 100% Selective Catalytic Reactions

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Students: 5 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding: $800,000

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 are to (1) fabricate three-dimensional or two-dimensional catalyst systems with complete control of catalyst anoparticle location, structure, thermal, and chemical stability; (2) 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; and (3) 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 2012 HIGHLIGHTS

- Chemical Transformations Mediated by Homogeneous Catalysis
- Chemical Transformations Mediated by Heterogeneous Catalysis

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

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Students:	7 Postdoctoral Fellow(s), 8 Graduate(s), 0 Undergraduate(s)
Funding:	$2,030,000

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, Robert G. Bergman, Christopher Chang, Enrique Iglesia, Kenneth N. Raymond, Gabor Somorjai, and T. Don Tilley—pursue independent research goals while extensively collaborating via joint supervision of graduate students and postdoctoral associates, and by extensively sharing instrumentation.

FY 2012 HIGHLIGHTS

- Model Catalyst Design by Colloidal Synthesis and their Studies for High Selectivity
- Reactivity Studies using Dendrimer-Encapsulated Late Transition Metal (Pd, And Pt) Nanoparticle Catalysts
- Time Resolved FT-IR and In-Situ Raman Monitoring under Catalytic Reaction Conditions
- High Pressure Photoelectron Spectroscopy for Catalysis Studies

Fundamentals of Heterogeneous Catalysis on Surfaces and Nanostructures

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Students:	3 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$1,660,000

PROGRAM SCOPE

The overarching goal of this proposal is to understand how structure and morphology of oxide and bi-functional catalysts affect their surface chemistry and catalytic properties particularly for reactions involving oxygenated molecules. Both model-oriented thin films of CeO_2 with different surface terminations and uniformly structured CeO_2 nanocrystals with specifically defined surface structures are used to explore structure effects and to tailor catalytic selectivity via structural differentiation. A second aim is to understand the role of metallic components and the synergism that arises in bi-functional catalysts in the reactions of oxygenates, especially as it relates to surface structure of the supporting oxide component.

FY 2012 HIGHLIGHTS

We have explored the role of surface structure, oxygen vacancies, and surface reduction upon the surface chemistry and catalytic selectivity of CeO_2. Adsorption and dissociation of water are found to be profoundly altered by variation in structure of the adsorption sites. Surface reaction, desorption products, and reaction selectivity in ethanol oxidative dehydrogenation reactions have been elucidated using CeO_2 nanoshapes that terminate in different crystallographic planes. Reaction and condensation of acetaldehyde upon a structurally defined $CeO_2(111)$ surface have been observed and explained by a combination of computation and experiment. The structure of TiO_2 supported Pt clusters has been determined computationally and is found to undergo a 2D-3D transition when more than 6-8 Pt atoms make up the cluster. The role of hydroxyl on the stability and energetics of Au clusters was also studied.

Organic Chemical Transformations at Interfaces

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Students:	0 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$1,100,000

PROGRAM SCOPE

The goal of this program is to gain a comprehensive understanding of the structure-reactivity relationships that control the kinetics, mechanisms, and product selectivity for the thermochemical and catalytic transformations of oxygen-containing molecules in the gas phase, in solution, and at solid metal oxide interfaces. The aims are to understand the role of oxygen functional groups involved in the kinetics of thermochemical transformations of organic model compounds, to understand the impact of organic-inorganic interfacial interactions upon free-radical and acid-catalyzed reactions, and to understand the influence of local nanostructure and interfacial environments upon molecular interactions, dynamics, and transformations. An integrated approach is employed that involves (1) synthesis of target model compounds, nanostructured mesoporous metal oxide supports and catalysts, and pore-derivatized hybrid materials; (2) determination of thermochemical and acid-catalyzed reaction rates, mechanisms, and product selectivities; (3) interrogation of the organic-inorganic interface by advanced solid-state NMR techniques and quasi-elastic neutron scattering to determine structure and dynamics; and (4) DFT theoretical studies and molecular dynamics simulations to analyze organic free-radical reaction pathways and to probe the structure and dynamics of the organic-inorganic interface. With this comprehensive approach, the research will significantly advance our understanding of the chemical transformations of oxygen-containing molecules, which will contribute to the design of improved catalysts for the selective conversion to fuels and chemicals.

FY 2012 HIGHLIGHTS

We have developed the first comprehensive kinetic model of the free-radical chain mechanism involved in the thermochemical decomposition of phenethyl phenyl ether. This research involved a combination of experimental pyrolysis investigations and extensive DFT calculations on the rates of individual mechanistic steps.

Understanding Ligand Protected Metal Nanoparticles for Catalysis

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Sr. Investigator(s):	
Students:	0 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$50,000

PROGRAM SCOPE

The overarching goal of this project is to understand the growth mechanisms, structure and bonding, and catalytic activity of ligand-protected metal nanoparticles by state-of-the-art computational tools. Ligand-protected metal nanoparticles often show well-defined structures and unique catalytic properties. However, the relationship between their structures and the catalytic activity is still lacking, and experimental efforts are still conducted on a trial-and-error basis. We will pursue three specific aims to address the overarching goal: (1) determine the nanoparticle growth mechanisms, (2) determine the origins of nanoparticle stability, and (3) learn how their catalytic activity correlates with their structure, size, and surface chemistry. For aim 1, we will employ both Monte-Carlo and molecular dynamics tools to investigate how metal atoms assemble into nanoparticles in the presence of organic ligands and why certain-sized nanoparticles have magic stability. For aim 2, we will focus on how organic groups interact with and protect the outside layer of the metal particles and how the interfacial bonding affects the electronic structure of the metal particle. For aim 3, we will use quantum mechanical tools to explore how the catalytic activity changes with the structure and size of the metal nanoparticles. By understanding the structure-property relationship of ligand-protected metal nanoparticles for catalysis, this FWP will address the second grand challenge identified in the BES Basic Research Needs Workshop for Catalysis for Energy for the “design and controlled synthesis of catalyst structures”. This research will also advance DOE’s missions in fuel cells and solar fuels, as metal nanoparticles are also used in electrocatalysis and photocatalysis.

FY 2012 HIGHLIGHTS

We have studied how halogen ligands interact with gold nanoclusters, and have predicted magic-number halogen-protected gold nanoclusters by an analogy to the well-established thiolated gold systems. For FY 2013, we will look at catalytic properties of these clusters for reactions such as selective oxidation.

Chemical Transformations at Complex Interfaces

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Rousseau, Roger, Pacific Northwest National Laboratory
Shaw, Wendy, Pacific Northwest National Laboratory
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Students: 15 Postdoctoral Fellow(s), 3 Graduate(s), 3 Undergraduate(s)
Funding: $4,176,000

PROGRAM SCOPE

This program's overall goals are aimed at the grand challenge of the control of chemical transformations by using catalysis. Research includes fundamental mechanistic studies of intermediates in hydrocarbon hydroprocessing, selective partial oxidation and simple acid-catalyzed reactions of hydrocarbons, electron/hole pair chemistry of a number of important surface reactions such as water splitting and hydrocarbon oxidation, CO_2 conversion, and enantiomeric selective reactions using novel bio-inspired stimulus-controlled catalysts. New theoretical approaches are developed and applied to characterize structural, electronic, and spectroscopic properties of catalysts and adsorbed reaction intermediates. These computational studies are intimately coupled to the experimental efforts in homogeneous and heterogeneous catalysis. In addition, the development of new multiscale computational methods is being pursued in order to accurately account for macroscopic catalytic performance. Novel catalyst synthesis methods are being developed and used to provide nano-dimensional catalysts with well-defined geometric and electronic structures, and new ‘operando’ experimental methods are being developed in order to provide the needed science for tackling catalysis grand challenges. The program is currently broken down into four subtasks: (1) catalysis by early transition metal oxides, (2) fundamental studies of heterogeneous photocatalysis on model TiO_2 surfaces, (3) surface science studies of the adsorption and reaction of CO_2, and (4) a modular energy based approach to molecular catalyst design.

FY 2012 HIGHLIGHTS

- Delocalized multi-center δ-bonding, that is, δ-aromaticity, represents a new mode of chemical bonding, which was first discovered as part of this program, enabling combined experimental and theoretical data this year that allows us to follow the evolution of the δ orbital as a function of O content.
- Reactivity/de-protonation energy (DPE) correlations were developed that can now be used as a "ruler" for solid acids to estimate DPE values (acid strength) and then structure of Brønsted acids with unknown structure.
- *In operando* NMR spectroscopic studies have shown that ruthenium tetraphosphine catalysts are not only among the fastest catalysts for CO_2 hydrogenation, but they are also equally effective as catalysts for the reverse reaction, dehydrogenation of formic acid.
- Recently, we have discovered a new water dissociation process on $TiO_2(110)$ surfaces that involves 'cross- row' proton transfer from a water molecule to an oxygen ad-atom through a bridging oxygen site.

Control of Hydrogen Release and Uptake in Condensed Phases

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Students:	1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$800,000

PROGRAM SCOPE

The objective of our research is to develop fundamental insight into small molecule activation in molecular complexes that will provide the basis for developing rational approaches in new catalysis design. Our focus is bi-functional (ambiphilic centers) molecular complexes comprised of both electron-rich and electron-poor sites, that provide an environment for heterolytic activation of molecular hydrogen and other small molecules such as CO_2 for transformation to fuels and for energy storage in chemical bonds. Our research team uses a combination of experimental and computational modeling approaches to study trends in structure-function relationships that control the thermodynamics and kinetics of small molecule activation. The outcome of the research will provide predictive models for controlling chemical transformations at the molecular level. This work has wide ranging implications in catalysis for energy storage and energy storage materials as well as alternative approaches to catalytic activation of small molecules without using transition metals.

FY 2012 HIGHLIGHTS

In our research we made significant progress on understanding the heterolytic activation of molecular hydrogen leading to the stabilization of protonic and hydridic hydrogen in Lewis acid Lewis base molecular complexes. Ammonium borohydride and ammonia borane, the prototypical Lewis acid Lewis base pair, provided an important background that has enabled us to extend our kinetic and thermodynamic studies in to more complex Lewis acid Lewis base complexes shown to activate molecular hydrogen in catalytic reactions. With our new focus towards optimizing the catalytic activation of hydrogen and other small molecules (e.g., CO_2, N_2), a wide range of new Lewis acid/base catalyst complexes are now under study to better understand the reactivity of these novel molecular structures for the catalytic reduction of polar substrates. In the past year, we have published a series of papers that describe new experimental and computational tools we have developed to gain fundamental insight into the reactivity of molecular complexes in solution that will enable the rational design of new catalytic transformations.

Early Career: Catalyst Biomimics: A Novel Approach in Catalyst Design

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Sr. Investigator(s):	
Students:	1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$500,000

PROGRAM SCOPE

The overall goal of this program is to incorporate a rationally designed proton channel into molecular catalysts for hydrogen production and oxidation. Proton channels, consisting of a series of proton relays, are essential for the rapid rates of proton reduction or hydrogen oxidation observed in enzymes such as hydrogenase, enzymes which are widely studied for their potential impact on energy and fuel storage. Using a combined experimental and computational approach, a peptide-based proton channel is being incorporated into $[Ni(P_2N_2)_2]$ catalysts to develop a fundamental understanding of how proton channels work and to ultimately enhance catalytic activity. Proton movement has been shown to be critical to the rate of these fast catalysts, yet incorrect proton movement is currently limiting their potential. The hypothesis of the proposed research is that providing a proton channel to and from the active site is an essential characteristic necessary to further enhance the activity of synthetic analogs. Using the Rosetta computational approach in collaboration with Dr. David Baker (U of Washington), potential peptide ligands with precisely positioned proton relays will be predicted. These will be synthesized, and the resulting structural and functional data will be utilized by Rosetta to refine the design in an iterative process. Attributes such as the pKa of the relays, the distance between relays, the rigidity, the structure and surrounding environment of the relay, and the number of relays will be tested. Additionally, we are utilizing DFT/metadynamics computational methods to understand the principles governing proton movement through the channel. Initially, the highly efficient proton channel of [FeFe]-hydrogenase will be studied, moving to our experimental systems as they are developed. 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. In the long term, if successful, the enhanced rates afforded by the proton relay system could allow these catalysts, made of inexpensive metals, to compete with and replace expensive Pt catalysts in fuel cells.

FY 2012 HIGHLIGHTS

We have appended small molecules to the $[Ni(P_2N_2)_2]$ catalyst to establish a two-relay channel. The proton movement through this channel is currently being evaluated. We are also incorporating structured peptides into the catalysts. The successes of these two approaches will allow us to begin incorporating structured peptides with a positioned proton channel and assess proton movement. We have also shown that water can act as a base to operate these catalysts, at similar overpotentials as triethylamine, providing a more environmentally benign substrate. Additionally, our initial evaluation of [FeFe]-hydrogenase has revealed the most likely proton channel for the enzyme, and we are currently investigating proton movement through that channel.

From Lignin to Hydrocarbon Carriers - Understanding and Controlling Scalable Catalytic Routes in Acqueous Phase

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Funding:	$500,000

PROGRAM SCOPE

The production of clean hydrocarbon-based energy carriers from lignocellulosic biomass involves a substantial number of sequential reduction, disproportionation, and elimination reactions that occur in a cascade mode, always in the presence of water. To successfully control the conversion process, it is essential to understand the possible ways to catalyze the reactions and understand how to control the access of reactants to catalytically active sites as a function of reaction progress. Towards this goal, the project focuses on understanding the catalytic chemistry in aqueous environments and at solid surfaces. The kinetics of key elementary reactions are analyzed to elucidate reaction mechanisms and the surface chemistry and state of catalyst materials are characterized under reaction conditions by in-situ spectroscopic methods together with theoretical and modeling studies.

FY 2012 HIGHLIGHTS

In operando X-ray Absorption Spectroscopy (XAS) was used to define the structure and composition of supported Pd nanoparticles during aqueous phase hydrodeoxygenation (HDO) of phenol: a model lignin-derived bio oil. The results show that the state and structure of the Pd are unaffected by water, acid, phenol (or its reduction intermediates), and the supports (C, Al_2O_3, or SiO_2). However, the nanoparticles changed slightly in size with the conversion of phenol caused by increasing absorption of hydrogen into the Pd lattice as phenol and unsaturated intermediates were consumed through reaction with hydrogen on the surface of the particles. First principles theory was used to interpret and simulate the observed states.

In-situ studies of the reaction of cyclohexanol on HBEA zeolite in liquid water at temperatures of up to 163 °C were initiated using high-resolution magic angle spinning nuclear magnetic resonance (NMR) spectroscopy. Researchers designed and fabricated a one-of-a-kind NMR rotor for the experiment capable of withstanding high temperature and pressure. The experiment enabled researchers to follow the reaction in real time and to discriminate between mechanisms for elimination of water from 1-cyclohexanol-^{13}C by virtue of being able to observe the rate at which the ^{13}C label redistributed in cyclohexanol and cyclohexene during the reaction. The results show that the E1 mechanism for dehydration of cyclohexanol on HBEA in water better explains the reaction products and kinetics. This is in stark contrast to the reaction in the gas phase where the E2 mechanism dominates.

New Bio Inspired Molecular Catalysts for Hydrogen Oxidation and Hydrogen Production

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Students: 3 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding: $620,000

PROGRAM SCOPE

Conversion between electrical and chemical energy is needed because of the temporal variations of renewable, carbon-free sources of energy such as solar and wind. Storing energy in the H-H bond of hydrogen is attractive since oxidation of hydrogen in a fuel cell provides electricity efficiently and cleanly. Electrocatalysts based on inexpensive, earth-abundant metals are needed since most fuel cells are based on platinum, an expensive, precious metal. The cost of cobalt, manganese, or iron is at least a thousand times less expensive than platinum, so dramatic cost savings would result from development of catalysts using these inexpensive, earth-abundant metals. We seek to obtain an understanding of the molecular reactivity that will allow us to design and discover new, robust, highly active molecular catalysts based on cobalt, manganese, or iron for oxidation and production of H_2.

FY 2012 HIGHLIGHTS

New cobalt complexes $[Co(P^{R}{}_{4}N^{Ph}{}_{2})_2(CH_3CN)]^{2+}$ (where $P^{R}{}_{4}N^{Ph}{}_{2}$ is a tetraphosphine ligand) were synthesized and fully characterized. These cobalt complexes are electrocatalysts for production of hydrogen by reduction of protons, with an optimized turnover frequency of 19,000 s^{-1} at 22°C. Thermochemical and theoretical studies show that the H-H bond is formed through protonation of a cobalt hydride. An iron complex with a bound H_2 ligand, $[CpFe(P^{Ph}{}_{2}N^{Bn}{}_{2})(H_2)]^+$, was found to catalyze H/D exchange between mixtures of H_2 and D_2, thus demonstrating that heterolytic cleavage of H_2 is occurring. This reaction models a key reaction observed in the [FeFe] hydrogenase enzyme in nature. Manganese complexes with pendant amines in the diphosphine ligand cleave the H-H bond reversibly and heterolytically, with the proton being transferred to a nitrogen and the hydride to the metal.

Center for Interface Science and Catalysis

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Nilsson, Anders, SLAC National Accelerator Laboratory
Students: 4 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding: $2,000,000

PROGRAM SCOPE

This Center addresses the fundamental challenges associated with the atomic-scale design of catalysts for chemical transformations of interest for energy conversion and storage. The goal is to combine experimental and theoretical methods to understand which properties control the catalytic properties of solid surfaces and to be able to use theoretical and computational methods to tailor new catalysts.

FY 2012 HIGHLIGHTS

The main results include the development of a new exchange-correlation functional for density functional theory calculations that include non-local correlation effects. The work has already opened up for the first quantitative description of hydrocarbons interacting with zeolites. Another milestone has been the identification of the active site in the industrial methanol synthesis catalyst system and the identification of new methanol catalysts. Combined experimental and theoretical work has provided a new understanding of trends in fuel cell catalysis and a new design principle for such catalysts. Finally, we have published the first database of surface chemical properties and software for anyone to access the data (suncat/slac/stanford/catapp).

Condensed Phase and Interfacial Molecular Science

Institutions Receiving Grants

Generation, Detection, and Characterization of Gas-Phase Transition Metal Containing Molecules

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Principal Investigator: Steimle, Timothy
Sr. Investigator(s):
Students: 0 Postdoctoral Fellow(s), 2 Graduate(s), 1 Undergraduate(s)
Funding: $119,000

PROGRAM SCOPE

The goal of this project is to determine the chemical properties of small transition metal containing molecules in the gas-phase. Gas-phase transition metal containing molecules serve as ideal venues for testing computational methodologies being developed to predict chemical properties of more extended metal-containing catalysis because the properties of these simple molecules can be precisely derived from high-resolution spectroscopic measurements. Particular emphasis has been placed on catalytically relevant platinum, Pt, iridium, Ir, rhodium, Rh, and gold, Au, containing molecules. The sensitivity required for detecting these ephemeral molecules is realized by use of laser induced fluorescence detection with photon counting techniques. Molecular beams of the molecules are generated via reacting laser ablated metal vapor with a supersonic expansion of a gaseous reagent (e.g., SF_6). The high spectral resolution garnered from cold (approximately 20 K) molecular beam generation and use of monochromatic laser sources assures extraction of the maximum information content. The determined properties include electronic state energies, bond lengths and angles, vibrational frequencies, permanent electric dipole moments, $\vec{\mu}_{el}$, magnetic dipole moments, $\vec{\mu}_m$, magnetic hyperfine interactions and radiative lifetimes. A knowledge of $\vec{\mu}_{el}$ and $\vec{\mu}_m$ is essential for developing schemes for kinetic energy manipulation (i.e., trapping) and enters into the description of numerous physical phenomena such as matter/light interaction. The spatial distribution and nature of the chemically relevant valence electrons are established from analysis of the magnetic hyperfine interaction, which is the interaction between the nuclear spins with the electrons. A comparison with theoretical predictions is used to assess the reliability of numerous computational methodologies being developed to model catalysis.

FY 2012 HIGHLIGHTS

The unique chemical properties of gold and platinum containing molecules are primarily associated with the large relativistic effects of Pt and Au. Accounting for these large relativistic effects is one of the most outstanding theoretical challenges and requires experimental input. Recently we have experimentally characterized the properties of *platinum monofluoride, PtF, and gold monofluoride, AuF.* A comparison with theoretical predictions illustrates that current relativistic treatments are insufficient even for these simple diatomic molecules.

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

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Students:	1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$149,000

PROGRAM SCOPE

The goal of this project is to achieve a detailed understanding of the properties of gas hydrates, with the focus on uncovering the mechanism, or pathway, of hydrate formation, and identifying the critical structures beyond which the process becomes irreversible, and upon which any attempts to control the process will primarily act. The pathway is a complex sequence of steps involving solvation, association, nucleation, growth, and a first-order-like transition, with a free energy barrier and unstable regime of thermodynamic states. Consequently, the theory of hydrate formation is in an early stage and computer simulations have been hampered by the rarity of rate-limiting visits to the barrier.

The project will exploit a new simulation algorithm, the generalized replica exchange algorithm (gREM), developed by the PI, which is optimized for sampling configurations separated by a large free energy barrier. Hydrate simulations will be performed in which unstable states along the formation pathway are robustly sampled and characterized, the critical configurations are identified, and the effect upon them of suppressants such as salts and methanol is determined. For a comprehensive attack on the problem, collaborators Profs Bill Klein (BU Physics) and Harvey Gould (Clark U Physics) will develop the nucleation theory of hydrates, emphasizing the techniques which they have developed.

FY 2012 HIGHLIGHTS

Dr. Edyta Malolepsza, postdoctoral associate, was recruited and began work on the project on September 1, 2012. Edyta is learning the gREM and has initiated simulations of phase equilibrium in a simple water model as background for introducing methane and beginning the hydrate studies. While preliminary, this work will be a significant contribution to the understanding of aqueous phase equilibrium. Joint Keyes/Klein/Gould group meetings have begun to coordinate simulation and theory and to share the distinct expertise of the various participants.

Single-Molecule Interfacial Electron Transfer

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Funding:	$188,000

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 understand 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. Single-molecule approaches are unique for heterogeneous and complex systems because the static and dynamic inhomogeneities can be identified, characterized, and/or removed by studying one molecule at a time. Single-molecule spectroscopy reveals statistical distributions correlated with microscopic parameters and their fluctuations, which are often hidden in ensemble-averaged measurements. Single molecules are observed in real time as they traverse a range of energy states, and the effect of this ever-changing "system configuration" on chemical reactions and other dynamical processes can be mapped. In our research, we have been integrating two complementary methodologies—single-molecule spectroscopy and near-field scanning probe microscopy (modified STM and AFM)—to study interfacial electron transfer dynamics in solar energy conversion, environmental redox reactions, and photocatalysis. The goal of our project is to integrate and apply these 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 electron transfer under ambient condition and electrolyte solution involving both single crystal and colloidal TiO_2 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 interface chemistry and physics.

FY 2012 HIGHLIGHTS

We have made significant advancement on studies of interfacial electron transfer dynamics in a dye-sensitized TiO_2 nanoparticle system by demonstrating and using a novel combined single-molecule photon-stamping spectroscopy and femtosecond transient absorption spectroscopy. Single-molecule photon-stamping technique and ensemble-averaged transient absorption spectroscopy provide efficient “zoom in” and “zoom out” approaches in probing the interfacial ET dynamics. The physical nature of the observed multi-exponential or stretched-exponential ET dynamics in the ensemble-averaged experiments, often associated with dynamic and static inhomogeneous ET dynamics, can be identified and analyzed by the single-molecule spectroscopy measurements.

Path Integral and Embedded Density Functional Theory Methods for Understanding Coupled Electronic and Nuclear Dynamics in Solar Photocatalytic Water Splitting

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Funding:	$115,000

PROGRAM SCOPE

We are developing new electronic structure and quantum dynamics methods to advance the fundamental understanding of coupled electronic and nuclear dynamics in solar photocatalytic water splitting. The rational design of molecular photosystems is a challenge of paramount scientific, industrial, and societal importance. Computational research has the potential to contribute in this area by allowing for detailed investigations of biological photosystems, by revealing key insights into fundamental photochemical processes, and by allowing for fast and inexpensive screening of candidate photosystems. However, major theoretical obstacles currently hinder the reliable and efficient computational modeling of photocatalytic processes. We are developing new methods that overcome the intrinsic challenges of simulating and understanding the dynamics of processes that are central to solar photocatalysis and basic energy science, including proton-coupled electron transfer (PCET) dynamics. Furthermore, we are using these new methods to elucidate the fundamental chemical processes at the heart of the photocatalytic water splitting, which will yield fundamental insights into natural photosynthesis, as well as new strategies for the design of biomimetic photocatalysts.

FY 2012 HIGHLIGHTS

Quantum dynamics methods for PCET reactions: Thus far, we have reported the first exact quantum simulations for condensed-phase models of PCET reactions (Mol. Phys., 2012). This work provides key insights into the PCET mechanism, important benchmark results for PCET reaction rates, and valuable analysis methods for characterizing reactive pathways in quantum systems. Additionally, we have completed a collaboration with Profs. James Mayer (U. Washington) and Harry Gray (Caltech), in which MD simulations and electronic structure calculations were used to understand anomalous experimental trends in the distance-dependence of PCET reaction rates (JACS, submitted). In the next period, we will report direct, all-atom simulations of PCET reactions using ring-polymer molecular dynamics.

Embedded density functional theory (e-DFT) methods: We have reported new methods to enable the accurate and scalable description of the electronic structure for reactive molecular systems in the condensed phase. In particular, we have reported a simple, exact e-DFT method that can be performed using standard electronic structure packages (JCTC, 2012); this paper is among the year's most highly-read for the journal. Also, we have reported improved methods for open-shell systems and transition-metal complexes (JCP, in press). In the next period, these methods will be used to study key PCET reactions associated with cobalt-containing catalysts for photochemical hydrogen reduction.

Electronic Structure of Transition Metal Clusters and Actinide Complexes and Their Reactivity

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Funding:	$121,000

PROGRAM SCOPE

Our projects deal with three areas of computational studies: the electronic structure of actinide complexes, carbon nanotubes and fullerene encapsulation of actinides, and subnano silver-metal clusters.

FY 2012 HIGHLIGHTS

We have made progress in (1) computing the binding properties of environmentally occurring actinides with carbon nanotubes and mesoporous silica as possible means of actinide sequestrations; (2) electronic structure and spectroscopy of subnano gold, silver particles, and alloys of silver and gold particles up to 25 atoms, which are found to have very interesting fluorescent emissions; and (3) properties of open 5d transition metal clusters especially tantalum. The research work on silver and gold nanocluster was carried out in collaboration with experimentalists. A significant part of our findings have been published or submitted for publication with a recent work being featured as a "hot paper" in Angewante Chemie, communications.

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

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

A summary for this program was not available at press time.

Early Career: Ultrafast Electron Transport Across Nanogaps in Nanowire Circuits

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Funding: $150,000

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. The first part of this program is concerned with developing highly sensitive tools for the ultrafast optical manipulation of tethered molecules through the evanescent surface field of plasmonic substrates. The second part of the program aims to use these tools for exercising control over the electron tunneling probability.

FY 2012 HIGHLIGHTS

One of the key technical challenges of this program is the ability to control surface fields to manipulate molecules on the ultrafast times scales. During the fiscal year of 2012, we have made great progress towards generating and manipulating such surface fields, called surface plasmon polaritons, with femtosecond light pulses. The resulting surface fields are pulsed in time and can be precisely controlled in terms of their duration, their energy, their spatial extent, and their location.

For instance, we have been able to concentrate the surface field in space to a small area of less than 0.6 µm wide and 2 µm long, and in time to width of less than 200 femtoseconds. Moreover, we have been able to generate such a surface field at two different colors. We accomplished this by manufacturing thin metal films that include special dual-color plasmonic lenses. These photonic devices enable multi-color optical manipulation of molecules that are placed in the probing area, performed entirely by plasmonic surface waves. We have shown that these devices produce strong, stable, and reproducible multi-color four-wave mixing (FWM) signals from nanoscopic test particles.

Non-Adiabatic Molecular Dynamics Methods for Materials Discovery

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Funding: $195,000

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 plan to develop a general-purpose code enabling 10-100 picosecond ensemble NAMD simulations for molecules and nano-sized clusters in the 100 atoms range at the level of hybrid time-dependent density functional theory. Our implementation will use atom-centered Gaussian basis sets and rigorously include non-adiabatic couplings between all relevant electronic states. Tully's fewest switches surface hopping algorithm will be employed for nuclear dynamics. The availability of such tools should dramatically accelerate the discovery of new energy-related molecular materials. We will combine 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. We plan to validate our methodology by comparison to accurate experiments and calculations. Demonstrative applications will include organic and transition-metal based sensitizers for solar cells and dyes for organic light emitting diodes.

FY 2012 HIGHLIGHTS

We have begun to compile a benchmark of photochemical product kinetic energy distributions from gas phase data. These benchmark data are presently being used to evaluate the accuracy of existing NAMD methods.

Spectroscopic Imaging Toward Space-Time Limit

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Funding:	$175,000

PROGRAM SCOPE

This project is concerned with the experimental challenge of reaching single molecule sensitivity with sub-molecular spatial resolution in optical spectroscopy and photochemistry. These experiments would lead to an understanding of the inner machinery of single molecules that are not possible with other approaches. Results from these studies will provide the scientific basis for understanding the unusual properties, processes, and phenomena in chemical and physical systems at the nanoscale. The experiments rely on the combination of the unique properties of lasers and scanning tunneling microscopes (STM). By using a low temperature scanning tunneling microscope (STM) and optics in the nano-junction, it has become possible to probe optical phenomena with sub-atomic resolution. Specific examples of such capabilities include the spatial dependence of multi-electron induced light emission and photo-induced desorption of single molecules, and the primary steps of electron transfer to a single molecule. In the conversion of sun light to energy and in optoelectronics, a promising scheme involves the use of nanoscale objects as the active media. The investigation of the fundamental mechanisms of how light can be efficiently coupled to molecules and nanostructures can not only lead to new scientific phenomena but also form the basis for new technology.

FY 2012 HIGHLIGHTS

Bond-selective chemistry, which involves selectively breaking and forming specific bonds, is one of the ultimate goals of chemistry. We succeeded to induce a sequence of target-selective bond dissociation and formation steps in a single thiol-based π-conjugated molecule adsorbed on a NiAl(110) surface at 10 K, using a scanning tunneling microscope (STM). We were able to selectively abstract different functional groups from the molecule step-by-step and monitor the evolution of the molecular electronic structure both in energy and real space at each reaction step. Furthermore, we form different types of Au-S bonds by manipulating and attaching a single gold atom to the sulfur atom at each end of the molecule.

Tunneling electrons have been shown to lead to light emission by coupling to plasmons in the nanocavity of the STM. By increasing the tunneling current, emission of light at twice and three times the energy of the tunneling electrons have been measured. The emitted light has a continuous distribution up to the energy corresponding to twice and three times the voltage bias between the tip and the sample and with spectral peaks associated with the nano-plasmonic modes of the metallic tip and the substrate. The observation of plasmonic emissions with multiple electron excitations raises the question regarding collective electronic modes associated with the metallic nanocavity of the STM junction.

Many-Body Effects in Transport and Energy Transfer

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Funding:	$152,000

PROGRAM SCOPE

Many-body effects are an important factor in predictions of properties of nano-materials and devices. Electron interactions with other electrons, electron-hole and plasmon excitations, and with nuclei give rise to a variety of measurable effects in transport and energy transfer on surfaces and interfaces. My research is focused on development of theoretical techniques to study open non-equilibrium molecular systems. Single molecules are used as building blocks of molecular devices for electronics, biosensors, nanoscale motors, controllable chemical reactivity and energy transfer. Sensitivity of molecules to reduction/oxidation/excitation makes tools of mesoscopic physics inconvenient, especially at resonance. Availability of developed methods of quantum chemistry and molecular spectroscopy for isolated molecular systems at equilibrium calls for development of techniques capable of utilizing these results to describe non-equilibrium molecular systems at surfaces and interfaces. Objectives of my research are:

(1) development of theoretical techniques capable of describing non-equilibrium molecular systems in contact with baths in the language of many-body states of isolated molecule;

(2) invention of approaches to describe electron-excitation interaction in realistic nonequilibrium molecular systems, including inelastic effects beyond simple perturbation theory and, for situations where Born-Oppenheimer approximation breaks down, optical response at non-equilibrium, and energy transport and transfer at surfaces and interfaces;

(3) incorporation of non-adiabatic molecular dynamics (NAMD) into molecular device response to driving force in a form alternative to Ehrenfest dynamics and time-dependent scattering theory—NAMD plays an important role in surface chemistry, radiationless transitions, and energy transfer at interfaces;

(4) development of practical approaches to simulation of strong molecule-contact correlation effects at non-equlibrium.

FY 2012 HIGHLIGHTS

Thus far, we had two important advances in formulating such theoretical techniques.

(1) We successfully generalized “the exact mapping” approach to inelastic transport. The former methodology, while completely general in description of electron-phonon coupling, is a single-particle scattering problem. Our formulation allows us to complement universality of the scheme with the information on many-body nature of transport in molecular devices. We demonstrate failure of the standard NEGF formulations for either strong electron-phonon interaction, or when assumption on time separation between molecular electron and vibration degrees of freedom breaks down.

(2) We formulated an exact powerful methodology for purely quantum consideration of collective plasmon-molecule excitations in nanojunctions. Such methodology is an important development, since any final goal for a realistic description of optical response in junctions should take into account molecule-plasmon interaction. Our approach is especially convenient in considerations of molecule-plasmon interactions in junctions, where combined coherent electron/energy transfer mechanisms play an important role in the observed physics. Note that a similar but approximate description within the standard nonequilibrium Green function formalism would require a fourth-order perturbation theory to take the effects into account.

Adsorption and Growth of Organic Materials on Metal Surfaces

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Funding:	$120,000

PROGRAM SCOPE

This proposal is about performing a detailed computational study of the adsorption and thin film growth of selected organic molecules on metal surfaces. The targeted systems are proposed to serve both as efficient energy harvesting devices (solar cells) and solid state lighting (light emitters). The goals of the proposed research include (1) providing an understanding of the correlations between the constituents of these organic materials and their interactions with metal surfaces (contacts) and (2) providing a set of computational tools to study their assembly, through a bottom-up approach, at different time and length scales.

FY 2012 HIGHLIGHTS

The PI finalized and submitted the Pc/Cu(110) paper; and the paper is now published [*J. Phys. Chem. C* 2012, 116 (44), pp 23465–23471]. In parallel, James Westover (student) started working on the adsorption of pentacene on vicinal surfaces. The first stage consisted on the adsorption on vicinals of Cu(100), namely Cu(511), Cu(711), and Cu(911). We have used DFT-PBE for these calculations. We found that the presence of a step increases the binding energy substantially and changes the bonding from physisorption on the Cu(100) surface to chemisorption on the vicinal surfaces. These results have been submitted in a paper to *J. Chem. Phys*.

The PI has also calculated the adsorption characteristics, using several vdW-DF implementations, of Benzene on coinage and transition metal surfaces. A paper is ready to be submitted to *Phys. Rev. Lett*.

Spin-Forbidden Chemical Reactions in Catalysis from First-Principles

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Funding:	$65,000

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.

Theoretical/Computational Studies of Fundamentals of One-Component and Alloy Metal Based Nanocatalysts Relevant to Alternative Sources of Energy

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Funding:	$78,000

PROGRAM SCOPE

The overall goal of this project is to develop an improved understanding of chemical reactions that are catalyzed by metal nanoparticles. We approach this problem by modeling representative reactions directly via first-principles, density functional theory (DFT) calculations. The model systems we study involve metal atom clusters of various size along with relevant reactant molecules. A specific objective of the project is to explore reactions on Pd and mixed Au/Pd clusters. The mixed-metal nanoparticles of these elements have been found to have a particularly strong catalytic activity for the production of hydrogen peroxide, an important "green" oxidant, from gas phase reactants. We use the DFT calculations to investigate various reaction parameters and how they are affected by particle size effects. Examples include the binding energies of reactant molecules adsorbed on the metal particles, preferred binding sites for adsorbates, and energetic barriers between steps in proposed chemical reactions. An interesting byproduct of the work is information regarding the evolution of the nanoparticles with increasing size. The insight gained via this research is expected to help guide the development of improved catalytic processes relevant to energy production, for example, the catalytic oxidation of lower hydrocarbons (e.g., alkanes) into alternative liquid fuels (e.g., methanol and ethanol).

FY 2012 HIGHLIGHTS

We continued studies of H_2 adsorption on Pd clusters. Building on our earlier characterization of optimal binding sites for single H_2 adsorbates, we considered saturation effects that arise from adsorption of multiple H_2 molecules. For example, while single H_2 molecules are found to adsorb dissociatively on Pd_N, additional H_2 adsorbates may bind molecularly. The transition from dissociative to molecular adsorption vs. coverage depends on cluster size. We also continue to be interested in the dielectric properties of small nanoparticles. We are investigating the question of metallicity by directly investigating how external electric fields are screened from the cluster interior by induced charge on the cluster surface. We do this using a technique for computing site-specific atomic polarizabilities developed in our group.

Chemical Imaging and Dynamical Studies of Reactivity and Emergent Behavior in Complex Interfacial Systems

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Funding:	$160,000

PROGRAM SCOPE

This program is exploring the efficacy of using molecular-level manipulation, imaging, and scanning tunneling spectroscopy in conjunction with supersonic molecular beam gas-surface scattering to significantly enhance our understanding of chemical processes occurring on well-characterized interfaces, including structurally-dynamic nanoscale catalytic substrates.

One program focus is on the spatially-resolved emergent behavior of complex reaction systems as a function of the local geometry and density of adsorbate-substrate systems under reaction conditions. Another focus is on elucidating the emergent electronic and related reactivity characteristics of intentionally constructed single and multicomponent atom- and nanoparticle-based materials. We are also examining emergent chirality and self-organization in adsorbed molecular systems where collective interactions between adsorbates and the supporting interface lead to spatial symmetry breaking.

In many of these studies, we are combining the advantages of scanning tunneling (STM) and atomic force imaging, scanning tunneling local electronic spectroscopy, and reactive supersonic molecular beams to elucidate precise details of interfacial reactivity that have not been observed by more traditional surface science methods. Using these methods, it will be possible to examine, for example, the differential reactivity of molecules adsorbed at different bonding sites in conjunction with how reactivity is modified by the local configuration of nearby adsorbates. At the core of this program resides the goal of significantly extending our understanding of interfacial atomic-scale interactions to create, with intent, molecular assemblies and materials with advanced chemical and physical properties. This ambitious program addresses several key topics in DOE Grand Challenge Science, including emergent chemical and physical properties in condensed phase systems, novel uses of chemical imaging, and the development of advanced reactivity concepts in combustion and catalysis including carbon management. These activities directly benefit national science objectives in the areas of chemical energy production and advanced materials development.

FY 2012 HIGHLIGHTS

We have had notable success in both instrumentation development and scientific achievement. (1) Nanoparticle Assembled Clusters and Materials: We are using local probes to interrogate and intentionally assemble atom and nanoparticle-based clusters to form extended ensembles that exhibit emergent electronic and chemical behavior. We have assessed the electronic structure of semiconductor nanoparticles using single-nanoparticle scanning tunneling spectroscopy. (2) Chiral Materials: We have continued to explore the formation of chiral interfaces using achiral molecular species adsorbed on chiral metallic crystals. (3) Spatially Resolved Surface Reactivity: We have been exploring the reactivity of adsorbed species as a function of local chemical environment using supersonic molecular beams and related molecular-level imaging using STM visualization.

Laser Dynamics Studies of Photoreactions on Single-Crystal and Nanostructured Surfaces

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Funding:	$121,000

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- and electron-initiated reaction mechanisms, half-collision dynamics, and other nonequilibrium-excited 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. We will use the tunneling current from the tip of our STM or an in situ flood UV lamp to excite adsorbate molecules at specific sites of these nanocrystals. The resulting chemistry and surface dynamics will be investigated via imaging of the reaction fragments in the vicinity of the reaction sites 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.

As a first step towards STM-based single-molecule dynamics studies, we have explored STM tip-induced dissociation of a series of linear aromatics on single crystal TiO_2 rutile(110) surface. We have successfully observed the structure of weakly adsorbed aromatics on TiO_2 surfaces and tunneling electron-induced bond cleavage within individual molecules.

FY 2012 HIGHLIGHTS

We have studied chemical properties of TiO_2 nanocrystals prepared on Au(111) substrate via a method developed earlier in our laboratory. Simple alcohols and 2-propanol in particular were used as test molecules. The results of temperature programmed desorption experiments were interpreted by comparison with the data obtained from single-crystal rutile(110) sample. The nanocrystals were shown to be more reactive than the single crystal surface, with both alcohol dehydration and dehydrogenation reactions observed, while only the former occurs on rutile(110). The next step will be to explore light- and STM tip-induced dynamics on TiO_2 nanocrystals using simple alcohols, carboxylic acids, or linear aromatics as probe molecules.

Photochemistry at Interfaces

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Funding:	$153,000

PROGRAM SCOPE

The objectives of our research program are to advance the development of a molecular-level understanding of the equilibrium and ultrafast chemical and physical properties of liquid interfaces using the interface selective second harmonic (SHG) and vibrational sum frequency (SFG) nonlinear optical spectroscopies. Femtosecond time-resolved SFG was used for the first time to probe a chemical reaction involving interfacial molecules pumped into their excited electronic states and probed with SFG. The ultrafast dynamics of electron transfer from ground state dimethyl anline (DMA) to photoexcited coumarin molecules at a water/DMA monolayer interface were obtained using femtosecond time-delayed pulses of light. The forward electron transfer, 16ps, was found to be twice as fast at the water/DMA interface than in bulk DMA. The faster rate is attributed to the lower reorganization energy at the interface due to the lower polarity at the interface, which was supported by the blue shifted electronic spectrum of coumarin obtained from our femtosecond SHG measurements.

The excited electronic state relaxation dynamics of molecules adsorbed to a colloidal microparticle surface were obtained for the first time by employing the pump-second harmonic probe method. The negatively charged colloidal particles used in these experiments were polystyrene sulfate, and the adsorbates were triphenylmethane malachite green (MG) molecules. The excited state lifetime of MG is dominated by radiationless decay from the excited singlet to ground state. It is the twisting motions of the aromatic rings about the central carbon atom that effects the excited state to ground state relaxation process. The decay time at the colloid interface was found to be 5.7ps, which is twice as long as in bulk water. The longer lifetime is tentatively attributed to the restricted motions of the aromatic rings due to the electrostatic interactions between the cationic MG and the anionic colloid.

FY 2012 HIGHLIGHTS

A major thrust of our work is the investigation of metallic nanoparticles, motivated by their unique optical, electronic, and chemical properties. We are currently using SHG to probe plasmonic effects on chemical equilibria and photophysical-photochemical processes at gold nanoparticle/water interfaces. Using SHG we have obtained the free energy of adsorption and the population of MG freely adsorbing to a 16 nm gold/water interface. The results are in good agreement with a modified Langmuir model, yielding an adsorption free energy that is approximately 4 kcal/mole more attractive than to polystyrene and oil droplets in water. The MG density on gold nanoparticles is 3 and 2 times greater. The origin of these difference are not known. One possibility that we are investigating is the contribution of the image charge interaction of the gold nanoparticle with MG to the adsorption free energy.

Plasmon Enhanced Photovoltaics: Modeling Energy and Charge Transfer in Solar Nanoassemblies

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

A summary for this program was not available at press time.

Super Instruction Architecture for Scalable Parallel Computations

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PROGRAM SCOPE

The Super Instruction Architecture (SIA) is an environment supporting creation of parallel software that yields high quality code with exceptional scaling and allows parallel programmers to be very productive compared to other approaches. The SIA comprises a domain-specific programming language, SIAL, and its runtime system, SIP.

The specific objectives of the project are threefold. (1) Extend the scaling performance of the SIA to 150,000 processors. This is being demonstrated in the context of ACES III, a software package for computational chemistry developed using the SIA. (2) Generalize and extend the specification and implementation of SIA to enable support for other application domains with minimal effort for developers. (3) Demonstrate the abilities of SIA in two applications relevant to Basic Energy Sciences.

FY 2012 HIGHLIGHTS

SIA System Enhancements: The SIA runtime system has been enhanced to support computation of contractions on a GPU. Continued efforts will focus on using static and dynamic analysis of SIAL programs to optimize scheduling on heterogeneous systems, and GPU implementations of additional computational kernels (super instructions). Proof of concept of a new worksharing abstraction which will allow scaling to extremely large numbers of cores has been implemented. The worksharing abstraction will take advantage of SIPMap, a tool that generates performance models from SIAL programs. The accuracy of SIPMap has been significantly improved. A new compiler for SIAL has been implemented that is easily adaptable to the different type vocabularies used in different domains and will support more sophisticated static analysis of SIAL programs. ACES III 3.0.7 was released on July 27, 2012.

Additional computational chemistry capabilities added to ACESIII include all variants of EOM electron attachment and ionization. ACES III was to investigate excited states of nucleobases. The study showed that only the equation of motion excitation energy coupled-cluster (EOMEE-CC) methods is accurate enough if the results with uncertainty of about 0.1 eV are desired and that triples corrections in the form of, e.g., the EOMEE-CCSD(T) method need to be included [Szalay, et al. J. Phys. Chem. A, 116, 6702 (2012)]. A follow on study extends this to nucleobases in their biological environment, considering hydration, glycoside bond, and base pairing [Szalay, et. al. J. Phys. Chem. A, in press, (2012)].

Using Plasmonic Nanoparticles for Improving Solar-Energy Conversion in Bacterio-Rhodopsin and other Systems

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Funding:	$144,000

A summary for this program was not available at press time.

Transition Metal Chemistry Studied with Cluster Ion Infrared Spectroscopy

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Funding:	$176,000

PROGRAM SCOPE

Transition metal-molecular complexes are studied in the gas phase to investigate the fundamental interactions at work in catalysis, metal-ligand bonding, and metal ion solvation. Cation-molecular complexes of the form $M_x^{n+}(L)_y$, where M= metals such as Fe, Co, Ni, Ag, Au in singly- or doubly-charged states, and L= molecules such as CO, CO_2, H_2O, C_2H_2, benzene, are produced in a supersonic molecular beam by pulsed laser vaporization. Specific clusters are size-selected with a reflectron time-of-flight mass spectrometer and their vibrational spectra are measured with infrared laser photodissociation spectroscopy. The vibrational shifts that occur upon ligand/adsorbate binding to metal, and how this varies with the number of ligands, determines the geometry and electronic structures of complexes, the number of ligands in the full coordination sphere around the metal, and the possible occurrence of insertion or ligand dissociation reactions mediated by the metal center. The experimental data is interpreted with density functional theory computations to provide new insights into metal-molecular chemistry.

FY 2012 HIGHLIGHTS

The focus of our recent work is infrared spectroscopy of transition metal cation complexes with carbon monoxide or carbon dioxide, e.g., $M^+(CO)_n$ and $M^+(CO_2)_n$. The carbonyl studies investigated the 18-

electron rule and its role in the coordination of early transition metals. Because these metals are relatively electron deficient, they require more than the usual number of four, five, or six ligands to achieve such an electronic configuration. Previous studies had shown that vanadium ions did not form a seven-coordinate complex, but both niobium and tantalum did, indicating a size effect of the metal ion. A similar study on titanium, zirconium, and hafnium species found that all formed 6-coordinate complexes having only 15 valence electrons. Rhodium carbonyls were found to form a stable 4-coordinate 16-electron species with a square-planar structure.

Metal-CO_2 complexes of vanadium were studied to investigate an unusual intracluster reaction suggested by our previous work on this system. New vibrations near 2400 cm^{-1} were observed to appear only when larger clusters were studied. However, the exact nature of the chemistry, if any, could not be established at that time because of the limited tuning range of the IR-OPO lasers available. New work extended the spectra over the range of 600-4500 cm^{-1}. Several new vibrational bands now appeared for clusters containing more than seven CO_2 ligands. These bands were assigned to an intracluster electron-transfer reaction activating CO_2 and producing an oxalate-type moiety in these clusters. This reaction is driven by solvation of the ion-pair that forms when more CO_2 ligands are present in the cluster. This reaction may be found for other transition metals, and studies are in progress to pursue this.

Room Temperature Single-Molecule Detection and Imaging by Stimulated Raman Scattering Microscopy

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PROGRAM SCOPE

The objective of the proposal is to achieve single-molecule detection sensitivity with near-resonance stimulated Raman scattering (SRS) microscopy. SRS microscopy was recently developed in our lab as a powerful technique for imaging heterogeneous samples based on their intrinsic vibrational contrasts, which provides much higher molecular specificity than absorption and fluorescence. The current sensitivity limit of SRS microscopy has not reached single molecule detection yet. We propose to capitalize on our state-of-the-art SRS microscopy and develop near-resonance enhanced SRS for single molecule detection.

FY 2012 HIGHLIGHTS

We have successfully demonstrated stimulated emission microscopy, single molecule absorption, and stimulated Raman microscopy based on a high-frequency modulation transfer technique. These first-of-a-kind new spectroscopy/microscopy methods tremendously improved our ability to observe molecules that fluorescence weakly, even to the limit of single molecule detection for absorption measurement. All of these methods employ two laser beams: one (pump beam) excites a single molecule to a real or virtual excited state, and the other (probe beam) monitors the absorption/emission property of the single. We extract the intensity change of the probe beam with high sensitivity by implementing a high-frequency, phase-sensitive detection scheme, which offers orders of magnitude improvement in detection sensitivity over direct absorption/emission measurement. However, single molecule detection based on fluorescence or absorption is fundamentally limited due to their broad spectral response. We tired to increase the sensitivity of stimulated Raman microscopy by taking advantage of resonance enhancement and have achieved detectability of ~10 molecules.

Towards 3rd Generation Organic Tandem Solar Cells with 20% Efficiency: Accelerated Discovery and Rational Design of Carbon-Based Photovoltaic Materials Through Massive Distributed Volunteer Computing

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Funding:	$322,000

PROGRAM SCOPE

The goal of this project is to extend the capability and scope of the Harvard Clean Energy Project (CEP)—our automated, high-throughput framework for the *in silico* screening and design of new organic photovoltaic (OPV) materials—to the complex material challenges of multi-junction OPV devices. These tandem solar cells offer, for the first time, a perspective to approaching 20% power conversion efficiencies with carbon-based materials which are otherwise known for their comparably low yield.

CEP allows us to characterize the electronic and optical properties of millions of potential OPV candidate structures at a first-principles quantum chemical level. In addition to the high-level electronic structure studies, we are also adopting strategies and techniques from the drug discovery community, cheminformatics, pattern recognition, and machine learning to assess the quality of our candidate compounds. It is thus ideally suited to finding molecular materials which fulfill the various requirements for the donor and acceptor phases in successful tandem OPVs. Our work utilizes distributed volunteer computing within IBM’s World Community Grid, which provides the project with a massive amount of computing time to survey the vast chemical space of organic electronics.

We believe that CEP is a powerful tool that can play a key role in the accelerated discovery of new carbon-based materials and can help to lay the foundation for rational design as well as inverse engineering in the future. The development of organic multi-junction solar cells is one of the new frontiers in renewable energy research, and our proposed work has the potential of providing important contributions to finding the next generation of organic electronic materials as well as to transforming the development process in materials science itself.

Multiscale Simulation of the Ground and Excited State of Molecular Triad in Polar Organic Solvent: Exploring the Conformations, Fluctuations, and the Free Energy Landscape

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Funding: $82,000

PROGRAM SCOPE

Molecular triad is an artificial analogue of a natural photosynthetic system that is composed of fullerene, porphyrin, and carotene functional groups. A multiscale simulation based on quantum chemical calculations and classical molecular dynamics simulations was employed to characterize the influence of structural fluctuations and dynamics of a polar organic solvent, namely tetrahydrofuran (THF), on the structural stability of the triad in the ground state and as well as in the excited charge-separated state. The excited state calculations on the triad were performed using two methods - an algebraic diagrammatic construction through second order method and a time-dependent density functional theory. Molecular dynamics simulations were performed on triad in a box of THF solvent with the replica exchange enhanced sampling technique. We have analyzed the free energy landscape, structural fluctuations, solvent orientations, static dielectric constant and the long-range electrostatic interactions between triad and solvent molecules. Our results suggest that the solvent arrangement is critical in stabilizing the structure of the charge-separated triad.

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

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

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.

(1) 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.

(2) 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 TiO_2 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 TiO_2 surfaces to investigate how the optical properties of the combined system emerge from its individual units.

(3) 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 we will 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 2012 HIGHLIGHTS

We investigated the optical properties of Cu_n(n=1-20) clusters within time-dependent density functional theory and compared our results with experiment and data on clusters of other group IB elements (Ag and Au) to develop chemical trends. Using classical Mie-Gans theory along with TDDFT computations, we predicted that if extremely oblate or prolate Cu clusters can be synthesized as metastable clusters, they will absorb very strongly in the lower end of the visible and IR region of the spectrum. The large absorption cross section and the tunability of the resonance energy by varying the aspect ratio of such chains (or nanowires) can be potentially important for future design of Cu-based nanomaterials for light-harvesting applications.

We also continued our studies involving the application of the GW-BSE method to noble metal atoms and clusters with occupied, yet shallow, *d* orbitals.

We have examined the shape, size, and exposed surface dependence of optical excitations in TiO_2 nanocrystals of sizes from 6 to 72 atoms and interpreted the results within the framework of the classical Mie-Gans theory.

Probing Catalytic Activity in Defect Sites in Transition Metal Oxides and Sulfides Using Cluster Models: A Combined Experiment and Theoretical Approach

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Funding:	$319,000

PROGRAM SCOPE

Our research program combines experimental and computational methods to study well-defined cluster models of heterogeneous catalytic materials. The focus of our studies has been transition metal oxide and sulfide clusters in non-traditional oxidation states (surface defect models) and their chemical/physical interactions with water and CO_2. We model H_2 production from photocatalyic decomposition of water, and photocatalytic CO_2 reduction 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, oxidation states, and structural features.

The general strategy is to (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; (2) measure the products and kinetics of cluster reactions with water or CO_2; (3) dissect reaction mechanisms computationally, to determine whether catalytically relevant interactions are involved; (4) benchmark computational studies by spectroscopic investigation of observed reactive intermediates; and (5) probe the effect of electronic excitation on bare clusters and cluster complexes, to model photocatalytic processes. The overarching goals are to identify particular defect structures that balance structural stability with electronic activity, and to find trends and patterns in activity that can lead to improvement of existing applied catalytic systems, or the discovery of new systems.

FY 2012 HIGHLIGHTS

Our recent studies have led to new insights into the relationship between metal suboxide structure and electronic properties. In particular, we identified the relative stability of M-O-M bridge-bond on the neutral surface when compared to the anion surface, implying that charge transfer from oxygen vacancies results in significant structural strain and/or reorganization surrounding the metal oxide surface defect. New computational results show what governs competition between H_2 production via $M_xO_y^- + H_2O \rightarrow M_xO_{y+1}^- + H_2$ and H_2 traps via $M_xO_y^- + H_2O \rightarrow M_xO_{y+1}H_2^-$. Computational studies on molybdenum oxide versus molybdenum sulfide clusters suggest lower reaction barriers and new reaction pathways between water and the metal sulfide versus oxide clusters. We have also completed new $M_xO_y^-$ + ROH reactivity studies that suggest H_2 production, and dual reactant studies, $M_xO_y^-$+ [CH_4 + H_2O], which show products of catalytic oxidation of methane by water accompanying H_2 production.

Understanding Nanoscale Confinement Effects in Solvent-Driven Chemical Reactions

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PROGRAM SCOPE

This project is addressing the fundamental question: *How does a chemical reaction occur differently in a nano-confined solvent than in a bulk solvent?* It is now possible to synthesize widely varying nanostructured porous materials ranging from sol-gels to supramolecular assemblies. One would like to design these systems for specific chemical purposes (e.g., catalysis or sensing) by controlling the cavity/pore size, geometry, and surface chemistry. To develop guidelines for this design, we must first understand how the characteristics of the confining framework affect the chemistry. Solvent-driven reactions, typically those involving charge transfer, should be most affected by confinement of the solvent; and thus our primary focus is on proton transfer, time-dependent fluorescence, and related dynamics. We are developing a unified understanding of chemical dynamics in the diverse set of nement frameworks, including nanoscale silica pores of varying surface chemistry.

FY 2012 HIGHLIGHTS

We have examined how liquid molecules rotate when confined within nanoscale frameworks by examining the reorientational dynamics of water, methanol, and ethanol in model silica pores. In this work, we have collaborated with Damien Laage, Ecole Normale Superieure in Paris. We have found that reorientation of water confined in hydrophilic pores exhibits a power law dependence at long times. This is related to the hydrophilic surface chemistry—in a hydrophobic pore, this behavior vanishes. In methanol and ethanol, the long-time decay appears to also exhibit a power-law decay, but this feature does not disappear in a hydrophobic pore. These results point to the differences in the fundamental reorientational dynamics of water and alcohols, suggesting that the methyl groups in the alcohols introduce steric effects that can alter the qualitative nature of the reorientation. We are continuing to examine these steric factors as well as the role of pore roughness.

Solvation dynamics in nano-confined solvents are generally marked by dramatic changes relative to the corresponding bulk solvent. In particular, long timescales not seen in the bulk solvent—often as long as hundreds of picoseconds or several nanoseconds—are observed in the time-dependent fluorescence signal. We have calculated the free energy for model solutes as a function of position in atomistic silica pores and found that the electrostatic interactions with the pore interface lead to a dependence of the solute position distribution on the solute dipole. Moreover, in hydrophilic silica pores, the fluorescence spectrum depends on the solute position. These results indicate that solute diffusion may contribute to the time-dependent fluorescence signal and, more generally, that it will be a component of the mechanism for a number of chemical processes in nano-confined solvents.

Modeling Molecular Electron Transport for Thermal and Photo Energy Conversion

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Funding:	$203,000

PROGRAM SCOPE

The goal of the research program is to enhance the control of charge transfer or transport through molecular scale interfaces. The understanding and control of charge transfer (CT) are essential for improving energy conversion applications. We develop electronic structure models to study (1) electron transfer processes that are important in photovoltaic applications, where CT follows absorption of light, and (2) electronic transport through molecular bridges, where the biasing is induced by a temperature gradient dropped across the bridge.

FY 2012 HIGHLIGHTS

We have investigated several key aspects of molecular bridges used in thermoelectric applications. We have studied the role of molecular end groups that anchor the molecules to the electrode(s). We elucidate the relationship between the end group and the charge transport mechanism (hole or electrons based). The sign of the thermopower (Seebeck coefficient) is determined by the alignment of the frontier electronic states of the bridge with the electrodes Fermi level. We showed that the end group induced polarization between the molecule and the electrodes determines the electronic structure alignment and therefore the thermopower. We have published the following manuscripts on thermoelectric properties of molecular bridges:

- End-Group-Induced Charge Transfer in Molecular Junctions: Effect on Electronic-Structure and Thermopower *J. Phys. Chem. Lett.*, 2012, *3* (15), pp 1962–1967
- Length Dependence of Frontier Orbital Alignment in Aromatic Molecular Junctions. Accepted App. Phys. Lett.

In another study, we investigate the source of “ghost transmission,” a numerical artifact that was implicated recently to skew electron transport modeling results. The “ghost transmission” was demonstrated upon model calculations where the bridge atoms are removed but their atomic basis functions are included in the calculation. We analyze the origin of the artifact and demonstrate that the artifact does not shift significantly the real transmission. Nevertheless, we provide guidelines for the design of artifact-free modeling of transport.

In another project, we study the role of range-separated hybrid (RSH) functionals in modeling CT processes in symmetric dimer systems. RSH functionals have been shown to properly treat CT states in donor-acceptor systems. We extend the benchmarking to off-site excitations in symmetric dimer systems that are related to CT, and analyze the effect of symmetry in the context of TDDFT. See

Examining Symmetry-Hidden Charge Transfer Excitations using Range-Separated Density Functionals H. Phillips, E Geva, and B. D. Dunietz *J. Chem. Theo, Comp.*, 8 (2012) 2661-2668.

Structural Dynamics in Complex Liquids Studied with Multidimensional Vibrational Spectroscopy

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Funding: $271,000

PROGRAM SCOPE

Water is a unique liquid due to the fact that it can form up to four hydrogen bonds, creating a loosely tetrahedral network of molecules whose connectivity evolves on ultrafast time-scales. It is the fluctuations of this network that allow water to rapidly solvate nascent charge and to participate in chemical reactions. The goal of our research is to develop ultrafast spectroscopic probes of the hydrogen bonding network of water and to use these probes to obtain a mechanistic understanding of how water dynamics influence proton transport in water and aqueous solvation.

Our specific interest is the mechanism by which water hydrogen bond dynamics mediates the structure and diffusion of protons in water. In the case of an excess proton (H+) or hydroxide (OH^- a proton hole), the transport of the ion is anomalously fast diffusion due to the ability to transfer a proton to or from neighboring water molecules, a process known as the Grotthuss mechanism. Simulations have suggested that hydrogen bond rearrangements play a key role in guiding proton transfer processes involving these ions. However, experimental work that is able to directly capture proton motion is lacking, due in large part to the difficulty of finding probes that can measure the timescales and mechanism of transfer.

FY 2012 HIGHLIGHTS

Our work during the past year has focused on the development of a 2D IR interferometer using broadband IR and initial applications to the study of water dynamics and proton transport in aqueous acids and bases. Ultrafast infrared spectroscopy is a powerful tool for studying proton transfer because strong aqueous acids and bases exhibit extremely broad and featureless transitions that span most of the mid-infrared region of the spectrum from ~900 cm^{-1} to 3400 cm^{-1} due to a large distribution of rapidly exchanging protonated configurations. To access all of these transitions in ultrafast time-resolved spectroscopy, we have developed the use of a broadband mid-infrared probe for use in nonlinear vibrational spectroscopy. By focusing 25 femtosecond 800 nm light pulses, together with their first two harmonics, in dry air, we can generate a plasma that radiates mid-infrared light which has spectral intensity from 4000 cm^{-1} down to the terahertz region and a pulse duration of <100 femtoseconds. These pulses are now being used as the probe pulse in two-dimensional IR spectroscopy and IR pump-probe experiments. In our initial experiments, we observe correlated spectral signatures of protons throughout the mid-infrared continuum that evolve on femtosecond times scales, validating the concept behind this proposal.

Theory of the Reaction Dynamics of Small Molecules on Metal Surfaces

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Funding:	$165,000

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 H_2. Initial studies of methane dissociation on Ni(111) 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 at the transition state for dissociation, the Ni atom over which the molecule dissociates would prefer to pucker out of the surface by a few tenths of an Angstrom. Thus, when this Ni atom 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 DFT studies on Ni(100), 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.

Recently, we have made significant progress using a formulation based on the Reaction Path Hamiltonian. In this approach, one locates the reaction (minimum energy) path for dissociation and performs 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). 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, we can examine the flow of energy between the various molecular and lattice degrees of freedom during the reaction. We showed that the symmetric stretch significantly softens at the transition state and is strongly coupled to the reaction coordinate. As a result, excitation of this vibration significantly increases reactivity, as observed by two experimental groups.

FY 2012 HIGHLIGHTS

Using these approaches, we have explored the dissociative adsorption of methane on Ni(100) and the highly-corrugated Pt(110)-(1x2). Our model was capable of reproducing and elucidating not only the reactivity of ground state and vibrationally excited molecules on Ni(100), but also the variation with lattice temperature as recently measured by the Utz group at Tufts. Studies on Pt(110)-(1x2) showed that lattice relaxation in the presence of the methane was far more complex than on smooth surfaces. In collaborations with groups in Leiden and Toulouse, we have also examined how lattice motion modifies H_2 dissociation on Cu(111) and the sticking of H atoms on graphene sheets, respectively.

Bridging the Gap between Quantum Chemistry and Classical Simulations for CO_2 Capture

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

PROGRAM SCOPE

We will develop a computational methodology based on quantum chemical calculations to obtain classical force fields that can be employed in simulations of CO_2 capture within metal organic frameworks (MOFs).

At present, the development of force fields for MOFs is still very empirical and relies on the availability of accurate experimental data. In the quantum chemical community, high-level methods have been developed which allow us to systematically study the nature of the various interactions. We will derive intermolecular potentials describing the interaction of CO_2 with MOFs directly from *ab initio* calculations. These potentials will offer the options of transferability and systematic improvement.

Our proposed developments are based on the NEMO (Non-Empirical Model potentials) approach to intermolecular forces.

Specific milestones of this proposal are:

(1) Benchmarking of the NEMO force fields against empirical and semiempirical force fields for well known MOFs. Up to now, the NEMO force field has been used successfully to determine only accurate structural properties of isolated molecules in solution. Since our long-term is to determine thermodynamic properties of gases in MOFs, and eventually to predict optimal material design, the first thing we need to check is if the NEMO force field parameters can determine energetic properties accurately. We will first develop CO_2-CO_2 parameters and MOF-CO_2 parameters for well-studied MOFs.

(2) Modification and refinement of the NEMO procedure to generate interaction potentials if the results of phase a) fail to be satisfactory. We do not expect the procedure to work smoothly at the first try. Rather there may be various complications. In the first instance, NEMO comprises a fitting step and

there is certainly a degree of arbitrariness associated with it. So we may have to reconsider the fitting scheme.

(3) Generation of force fields for MOF-based materials which have not yet been studied experimentally in order to predict adsorbtion properties of these new materials. We will study Mg_2(dobdc) (dobdc^{4-} = 1,4-dioxido-2,5-benzenedicarboxylate; Mg-MOF-74, CPO-27-Mg), which has a small surface area but presents a high density of exposed metal cation sites following activation and the analogue one with Zn instead of Mg. We will investigate the adsorption of various gases within these MOFs to identify which framework properties are responsible for the favorable CO_2 uptake and selectivity. If the procedure is successful, we will generalize it to different MOFs in which the various components will be varied.

(4) Extension of the procedure to more chemically diverse systems, like ionic liquids. Also, here the idea is to tailor-make ionic liquids for optimal performance; similar to the situation for MOFs, the number of possible materials is orders of magnitudes larger than can be realistically synthesized and we will use our methodology to make prediction of possible interesting materials.

Developing Advanced Methods for Excited State Chemistry in the NWChen Software Suite

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Funding:	$486,000

PROGRAM SCOPE

A suite of new theoretical methods will be 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, from 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 and at the SciDAC Institute for Sustained Performance, Energy, and Resilience.

FY 2012 HIGHLIGHTS

As funding for this project began in the last month of the fiscal year, progress in FY 2012 was limited to attending the kick-off meeting for the SciDAC-3 application projects, held in Rockville, MD, September 10-12, 2012, and planning for activities at Minnesota and Pacific Northwest Laboratories, undertaken in partnership with SciDAC institutes. The work to be undertaken in FY 2013 includes implementing generalized Born solvation models into NWChem together with associated vertical electrostatic models for predicting excited-state absorption and emission solvatochromism. Longer-range, we will consider how to merge these calculations with real-time evolution of a time-dependent density functional theory excited state, taking special advantage of PNL expertise in this area. We will also implement complete-active-space (CAS), restricted-active-space (RAS), and related new multiconfiguration self-consistent-field variations, and post-CAS, -RAS, etc., second-order perturbation theory models into NWChem, taking advantage of experience with parallel coding efforts in other software. Finally, enhanced sampling schemes will be explored through collaboration with the QUEST SciDAC institute (working on Uncertainty Quantification).

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

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	Neaton, Jeff, Lawrence Berkeley National Laboratory
	Sholl, David, Georgia Tech Research Corp
	Smit, Berend, California-Berkeley, University of
	Snurr, Randall, Northwestern University
	Tsapatsis, Michael, Minnesota, University of
	Yaghi, Omar, Lawrence Berkeley National Laboratory
Students:	6 Postdoctoral Fellow(s), 10 Graduate(s), 4 Undergraduate(s)
Funding:	$2,184,000

PROGRAM SCOPE

We will create a Nanoporous Materials Genome Center (NMGC). The NMG will be organized around a novel class of materials, namely metal-organic frameworks (MOFs), that have many interesting properties and offer high-payoff opportunities from a computational design point of view.

The NMGC will develop and employ state-of-the-art computational tools to characterize and predict the performance of millions of as-yet-unsynthesized materials and it will provide a repository of experimental structures and associated properties. The NMGC, continuously validated against experiment, will serve to integrate materials discovery, materials design, materials characterization, and functional performance.

The Center will bring together eleven theoretical chemists and chemical engineers and four experimentalists, whose combined expertise will cover all areas needed for a unique collaborative effort.

The following chemical challenges will be addressed: (1) Separation of N_2/O_2 in open-site MOFs; (2) Separation of N_2/CO_2 in amine containing MOFs; (3) Stimulus-responsive materials; (4) Alkane activation in MOFs; and (5) MOFs containing metal ions in unprecedented coordination environments.

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

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Funding:	$115,000

PROGRAM SCOPE

The overall goal is to improve the reliability and performance of time-dependent density functional theory (TDDFT)-based methods for the description of coupled electron-ion dynamics, which is critical for reliable predictions of modeling and design of solar-cell devices. Both the purely electronic side—electronic excitations and time-resolved dynamics—as well as the electron-nuclear coupling side have challenges that will be addressed. Robust non-empirical exchange-correlation functionals will be developed for charge-transfer processes, both in the linear response regime for computing spectra as well as in fully time-resolved non-linear descriptions of charge transport. The question of modeling the exchange-correlation potential for dynamics ensuing from an initially excited state, which has been largely neglected in the literature so far, will be addressed. Exactly solvable model systems will be used to help derive the form of the functionals to build in the correct physics. A new semiclassical treatment of nuclear dynamics coupled to TDDFT electrons, based on using Ehrenfest backreaction for trajectories composing the semiclassical nuclear wavefunction, will be explored and should overcome some of the limitations of the presently-used methods (including lack of branching and electronic relaxation). In parallel, rigorous semiclassical analyses of the nuclear wavefunction in an exact factorization of the molecular wavefunction will aid our understanding of how electron-nuclear correlation operates.

FY 2012 HIGHLIGHTS

This project is relatively new, with a start-date of Sep 1, 2012. The main highlight so far involves an exact time-resolved study of charge-transfer, in collaboration with Angel Rubio’s group in San Sebastian, Spain. By exactly solving for a one-dimensional two-electron model of a molecule, we found that as an electron transfers between closed-shell molecular fragments at large separation, the exact correlation potential gradually develops a step and peak structure in the bonding region. This structure has a density-dependence that is non-local, both in space and time; even the exact ground-state exchange-correlation functional fails to capture it. When charge transfers between open-shell fragments, an initial step and peak vanishes as the charge-transfer state is reached. We showed that lack of these structures in usual approximations leads to dramatically inaccurate charge-transfer dynamics. Our next step is to try to derive a non-adiabatic non-local correlation functional that captures these features. This work has been submitted for publication, and a preliminary version can be found at http://arxiv.org/abs/1211.2849 (authors: J. I. Fuks, P. Elliott, A. Rubio, and N. T. Maitra).

Computational Modeling and Theory Development of Energy and Charge Flow Dynamics in Photosynthetic Units and Conjugated Polymer Systems

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

PROGRAM SCOPE

The goal of the program is creating new impetus in the development of organic or bio-inspired solar energy conversion devices through theoretical research on both natural and synthetic systems. On one hand, efforts have been made to provide new theoretical insights into the design principles of natural photosynthetic systems by modeling and calculating their spectroscopic data. On the other hand, new theory development and applications have been made so as to elucidate correct mechanism and reliable quantitative description of energy/charge transfer processes in organic conjugated molecules. In the long term, these efforts will be integrated so as to lay out key factors and design principles that can lead to efficient and robust energy and charge transfer processes in synthetic systems.

FY 2012 HIGHLIGHTS

The progress made during the last funding period consists of the following four areas: calculating the emission lineshape of the light harvesting 2 (LH2) complex of purple bacteria, theory of inelastic coherent resonance energy transfer, theory of four wave mixing spectroscopy, and new theoretical formulation of nonadiabatic quantum dynamics in the basis of adiabatic electronic states.

For the emission lineshape of LH2, a complete expression within the second order quantum master equation approach was derived and tested. This accounts for the effects of exciton-phonon entanglement and their nonadiabatic contributions, and results in desired phonon band on the red side of exciton-peaks. This has been a critical step in calculating the energy transfer rate between LH2's, which will be one of the main research projects during the next funding period. A paper reporting the results was submitted to the Journal of Chemical Physics on Nov. 24, 2012. A theory of coherent resonance energy transfer including inelastic effects was developed and published. The theory helps to understand how quantum mechanical torsional or distance modulation of flexible organic molecules influences the coherent resonance energy transfer dynamics. A new theoretical formulation developed and published recently offers methods to calculate two dimensional electronic spectroscopy signals solving quantum master equations in multiple steps. A comprehensive theoretical formulation was published recently for the special issue on nonadiabatic dynamics in the Journal of Chemical Physics. This work exposes important but often neglected theoretical issues in combining first principles electronic structure calculation with known quantum dynamics approaches, and formulates a method to conduct dynamics calculation directly employing the information on the adiabatic electronic states. Overall, the advances addressed above either have helped better understanding of energy or charge flow dynamics or will help more reliable and quantitative modeling in the future.

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

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Funding:	$150,000

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.

One of the key issues in the simulation of the aqueous environment is the accurate description of liquid water within the density functional theory. A large portion of the work will be devoted to understanding the sources of error in the simulations. The structure and dynamics of aqueous electrolytes at metallic interfaces, taking into account the effect of the electrode potential, will be studied in detail. The electrode potential will be set by using the methodology already developed for the study of electronic transport in nano-structures. The proposed research will involve the tuning of DFT-based methods to allow the performance of efficient and accurate ab initio molecular dynamics of metal-electrolyte interfaces.

FY 2012 HIGHLIGHTS

We have made significant advances on the description of the water-metal interface. We have been able to perform ab initio molecular dynamics simulations of water adsorbed onto a biased palladium electrode. The results show that the structure of the water at the interface is very sensitive to the bias sign. We also see that water dissociation is not achieved for the range of bias studied.

In addition, we have published a paper [Phys. Rev. Lett. 108, 193003 (2012)] that shows nuclear quantum effects in ice are rather anomalous. The study hints that these effects could be also relevant in liquid water.

Optimizing Interfacial Charge Transfer in Photocatalytic Water Splitting Devices

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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

The goal of this proposal is to explore the role of water dissociation and facilitated proton diffusion through and out of the surface of semiconductors with photocatalytic activity. In particular, we have focused on understanding why GaN is such a good catalyst for water oxidation. The goal of the program is to identify why aspects of a given semiconducting surface are critical to improving the oxidation rate of water.

FY 2012 HIGHLIGHTS

We have explored in detail the dissociation and proton transfer mechanisms at the non polar surface of GaN (10-10). Among the main conclusions from our study we cite the following: (1) For water dissociation to occur at the surface, ionic species that act as Lewis acids and Bronsted bases must exist at the surface. This is the same as saying that ionic charges of different sign must be present. Non polar semiconducting surfaces satisfy this requirement. (2) The local atomic charges of the atoms at the surface are critical for inducing dissociation. (3) The geometry of the surface atoms is also important. The lattice parameter of GaN makes the distance between Ga-Ga atoms at this surface favorable to the formation of H-bonds between hydroxyl groups. (4) The non dissociative Ga sites at the surface have unsaturated bonds and are positively charged, representing an attractive potential for lone pairs in water molecules, which make strong H-bond-like bonds with these Ga atoms. These H-bond-like bonds are so strong that water molecules can now dissociate into Ga-OH- and H+, which are delivered to the bulk. (5) These non-dissociative Ga surface sites are responsible for the low surface Pka, which we have estimated to be ~3. The surface is very acidic but with a very different deprotonation reaction as compared to the standard deprotonation observed in oxide surfaces.

Single Molecule Chemical Imaging at Femtosecond Time Scales

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Students:	4 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding:	$600,000

PROGRAM SCOPE

Imaging molecular functionality with atomic spatial resolution and ultrafast temporal resolution will enable improved understanding of light-matter interactions and thus has the potential to impact the design of photovoltaic, photosynthetic, and photocatalytic materials and devices. While ultra-high vacuum (UHV) scanning tunneling microscopy (STM) can image and manipulate single molecules with atomic precision on surfaces, its temporal resolution is typically limited to the millisecond bandwidth of current preamplifiers. On the other hand, pump-probe spectroscopy with ultrafast lasers can routinely achieve femtosecond temporal resolution. In addition, chemical fingerprinting can be achieved with vibrational spectroscopies such as surface-enhanced Raman spectroscopy (SERS). However, these optical techniques struggle to overcome the diffraction limit, which often implies spatial resolution at the micron scale. Our SISGR team seeks to overcome the respective limitations of UHV STM and laser spectroscopy by integrating these techniques into one experimental platform. Significant progress has been made, including the demonstration of surface-enhanced femtosecond stimulated Raman spectroscopy (SE-FSRS) and ultra-high vacuum tip-enhanced Raman spectroscopy (UHV-TERS). In parallel, new surface chemistries have been developed, such as organic self-assembled monolayers stabilized via cooperative hydrogen bonding, surface photopolymerization, covalently modified graphene, and molecular *p-n* junctions based on pentacene and fullerenes. Since the systems and substrates chosen for this work are directly applicable to dye-sensitized solar cells, organic photovoltaics, and photocatalysis, this research program has provided insight into emerging energy technologies and has impacted the fundamental scientific goals outlined in the DOE Grand Challenges.

FY 2012 HIGHLIGHTS

A primary goal of this SISGR program is the development of tools and techniques that enable ultrafast Raman spectroscopy with single molecule sensitivity. Toward this end, progress has been made in two primary areas over the past fiscal year:

(1) SE-FSRS: A proof-of-principle experiment on SE-FSRS demonstrated a significant advance in combining the fields of plasmonics and ultrafast spectroscopy. Briefly, the plasmonic focusing of electromagnetic fields long used for SERS have been integrated with the ultrafast structural technique of FSRS. Using a 100 kHz amplifier, SE-FSRS was successfully demonstrated on Au plasmonic nanoantennas with approximately 0.5 monolayers of *trans*-1,2-bis(4-pyridyl)ethylene (BPE) as the adsorbate.

(2) UHV-TERS Integrated with Molecular-Resolution UHV-STM: Raman spectra consisting of multiple vibrational modes have been acquired using UHV-TERS. Using a plasmonic Ag tip and 633 nm continuous wave laser illumination of the UHV STM tip-sample junction, eight vibrational modes were resolved in the TER spectra for copper phthalocyanine (CuPc) adlayers on Ag (111). Concurrently, sub-nanometer

molecular resolution STM images were obtained, revealing subtle features in the CuPc adlayer, including the orientation and boundaries between ordered molecular domains.

Surface Plasmon Enhanced Chemistry

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Students:	2 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding:	$285,000

PROGRAM SCOPE

Surface plasmons (SPs) are collective excitations of conduction electrons near the surfaces of metallic structures. The intense and strongly varying fields they generate offer opportunities not only for enhancing spectroscopic processes such as Raman scattering, but actual chemical change. This grant is a joint activity by George Schatz and Mark Ratner at Northwestern University directed at the theory, computational methods, and modeling of chemical processes that can be enhanced or guided via SPs. Included in these studies is theory and code developed in which computational electrodynamics methods, electronic structure methods, and electrodynamics coupled to quantum mechanics is used to study spectroscopic and optical properties, including extinction, scattering and Raman spectra, transmission of light through metal films, near-field imaging, nonlinear effects, optical forces, photoelectron angular distributions, and plasmon mediated electron transport. Also included are applications aimed at understanding how plasmon excitation can influence and enhance chemical processes that range from simple photochemical reactions to electron transport devices and nanoparticle synthesis.

FY 2012 HIGHLIGHTS

Projects completed through October 2012 included (1) studies of nanoparticle electrodynamics to develop better software and to model experiments concerned with such fundamental issues as hot spot formation, size-dependent dielectric properties, and dipole-reradiation effects; (2) electronic structure theory development aimed at methods that can determine dielectric functions for plasmonic materials, and mixed quantum/electrodynamics methods; and (3) initial work concerned with coupling of electronic excitation to phonons and to heat in the surrounding solvent. Our electrodynamics work demonstrated that electromagnetic hot spots at nanoparticle junctions are often associated with dark plasmon modes, which is an important issue for optimizing plasmon-enhanced chemical processes. We also demonstrated that at least for single-crystal silver nanoparticles, scattering of conduction electrons from the nanoparticle surfaces can be coherent, which means that plasmon damping is not necessarily more significant for smaller particles as is commonly assumed. Our new method for calculating dielectric functions provides a parameter-free method that we successfully used in applications to the In-Ga liquid metal alloy. Our work on coupling electrodynamics and quantum mechanics has progressed to a theory that includes both passive plasmon enhancement and the static limit of chemical enhancement mechanism for spectroscopic measurements such as SERS. Finally, we are actively engaged in a new project where we are working with experimentalists to model femto-second pump-probe measurements of electronic relaxation leading to phonon excitation and decay to heat.

Reaction Field Model for Treatment of Solvation in Electronic Structure Calculations

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

PROGRAM SCOPE

The objective of this program is to develop a comprehensive reaction field model and accompanying computer program to enable accurate and efficient treatment of solvation effects in electronic structure calculations on chemical and spectroscopic properties of a solute, with particular application to water. Building on an existing modern dielectric continuum model of long-range electrostatic interactions that properly takes into account the quantum mechanical nature of the solute, additional models are being developed to specifically describe the remaining short-range solute-solvent interactions such as hydrogen bonding, exchange repulsion, and dispersion attraction. A major goal is to keep the number of empirical parameters in the models to a minimum by using physically-based expressions for the various contributions. The resulting overall model can stand alone as a very efficient means to carry out useful calculations on chemistry in solution, and may also serve as a valuable coarse-grained stage for screening purposes to be followed by more computationally intensive studies on specific aspects.

FY 2012 HIGHLIGHTS

A simple implicit model of the solvation energy arising from hydrogen bonding interactions between a solute and water solvent has been developed. This model expresses the hydrogen bonding energy in terms of the maximum and/or minimum values of the normal electric field produced by the solute at the surface of the cavity that excludes the solvent from the solute region. This dependence is quite nonlinear, such that the hydrogen bonding energy is found to be a constant times the field extremum raised to a power in the range of 3-4.

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

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Funding:	$142,000

PROGRAM SCOPE

The goal of this project is to develop electronic structure methods for large systems, with a target of obtaining “chemical accuracy” of about 1 kcal/mol or better, yet where the method is still affordable enough to be applied to geometry optimizations and *ab initio* molecular dynamics simulations for systems containing hundreds of atoms. Two avenues toward this goal are being pursued simultaneously. First, we are developing a many-body extension of symmetry-adapted perturbation theory (SAPT) that is designed for rapid and accurate computations of intermolecular interactions energies. Second, we are developing fragment-based quantum chemistry approaches based on partitioning a large system into overlapping fragments. By performing a large number of small electronic structure calculations (which are therefore amenable to massively-parallel architectures), we aim to approximate the original supersystem's energy to very high accuracy but with very low wall for performing the calculations.

FY 2012 HIGHLIGHTS

By replacing the SAPT dispersion formulas with empirical dispersion potentials and employing Kohn-Sham density functional theory to describe monomer electron correlation effects, we have developed a method for computing intermolecular interactions in clusters whose cost is cubic scaling, both with respect to monomer size and with respect to the total number of monomers. The accuracy of this approach for neutral monomer units is better than 0.5 kcal/mol, which is as good or better than existing electronic structure approaches whose cost is $O(N^5)$ or $O(N^6)$ with respect to the size, N, of the entire cluster.

Computational Design of Metal Organic Frameworks for Photocatalytic Reduction of CO_2

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Students:	1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$71,000

PROGRAM SCOPE

This is a joint project with Prof. James Lewis in the Department of Physics at West Virginia University. The main objective of this project is to explore new porous coordinated polymer materials that exhibit photoactive properties. Such materials will yield a number of benefits where the absorbed sunlight can be used in the PCP framework to perform a desired effect. For example, we are currently exploring PCPs that will reduce CO_2 utilizing sunlight energy from a photocatalytic PCP material. As part of this combined project, the Lewis research group is focusing on developing non-adiabatic molecular dynamics simulation tools within FIREBALL (a local orbital based density functional theory method) so that we can understand the charge excitation dynamics in photoactive PCP materials. Additionally, we are working jointly to understand some catalytic properties of published PCPs; we are using umbrella sampling (molecular dynamics) within FIREBALL to obtain the free energy barriers associated with a chosen reaction coordinate. Our research is strongly coupled with two chemical synthesis research groups (Christopher Matranga at the National Energy Technology Laboratory and Professor Hongcai Zhou at Texas A&M University) so that we are pursuing materials that are directly relevant to their synthesis and characterization.

FY 2012 HIGHLIGHTS

We have studied the adsorption and diffusion of CO_2 in nanoporous materials using a combination of classical molecular dynamics and plane wave periodic density functional theory (DFT). We have used DFT to compute entrance barriers for CO_2, H_2, and CH_4 in order to assess selectivity. We have identified pores that allow selective adsorption of CO_2 over CH_4. We have then modeled adsorption of CO_2/CH_4 mixtures from the gas phase using classical molecular dynamics. We find that the pore entrances we investigated were able to allow CO_2 adsorption and effectively inhibit CH_4 adsorption with very high selectivity. Likewise, H_2 was selectively adsorbed over CH_4. This paper was accepted for publication in the *Journal of Physical Chemistry* (DOI: 10.1021/jp3098022). We have also studied reactions in a porphyrin MOF that has been experimentally studied by Hupp and coworkers. The Mn-porphryin MOF that Hupp et al. studied is one of a very few MOFs that have been shown to have high catalytic activity. We have modeled the reaction process for styrene oxidation within this material and have identified the reaction pathways and barrier heights using a combination of the dimer method and the nudged elastic band method. The reaction pathways were observed to involve significant changes in spin states for the lowest energy paths. We have a draft manuscript that is nearing completion that will soon be submitted.

Critical Evaluation of Theoretical Models for Aqueous Chemistry and CO_2 Activation in the Temperature-Controlled Cluster Regime

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Funding:	$110,000

PROGRAM SCOPE

Our joint program integrates experimental and theoretical methods to exploit the unique properties of isolated cluster ions as media in which to quantify the molecular-level interactions underlying the cooperative behavior of solvent networks such as that found in liquid water. This involves determining the structures of neutral and charged water clusters both as a homogeneous solvent and embedded with solutes corresponding to labile intermediates in radiation-damaged systems. The goal is to provide benchmarks that calibrate both density functional and *ab initio* methods, as well as model approaches that can handle larger systems and longer time scales. The measurements are carried out using custom instrumentation involving freezing out local minima with Ar-mediated cluster synthesis and structurally characterizing them through theoretical analysis of their vibrational predissociation spectra. We have recently dramatically expanded the chemical scope of our “bottom-up” approach by integrating a temperature-controlled ion processing capability that can sample complex molecules directly from solution using electrospray and other ionization schemes. An example of the information that can be obtained with our approach is our identification of the structural motifs that water networks adopt in accommodating an excess electron. Another ongoing focus is to elucidate the underlying mechanics of water behavior that is obscured in measurements on the macroscopic system. Our approach involves monitoring the temperature-dependent spectral diffusion of isotopically labeled water clusters. A new direction for our efforts involves addressing the properties of ionic liquids that are responsible for their role as solvents for the catalytic activation of CO_2.

FY 2012 HIGHLIGHTS

We unraveled the molecular-scale mechanics of solvent-mediated electron scavenging. This was achieved using Ar-assisted condensation to trap a neutral CO_2 molecule on a negatively charged water cluster to prepare the $CO_2{\cdot}(H_2O)_6^-{\cdot}Ar$, “entrance channel” complex. Infrared vibrational excitation of this meta-stable assembly then triggered the water network deformations, leading to formation of the microhydrated CO_2^- radical anion. Molecular dynamics simulations of this reaction then elucidated the specific network rearrangements that lead to eduction of the CO_2. These results were published as a cover article in *J. Phys. Chem. A*. Another completed project involved elucidation of the microscopic mechanics of excess electron attachment to the multiple H-bond bridge at the heart of radiation-induced DNA damage. This was accomplished using the formic acid dimer anion, $(HCOOH)_2^-$, as a model system where we could follow the intracluster, electron-induced proton-transfer event. The spectroscopic signature of the proton-transferred species was rationalized based on the anomalous solvatochromic response of the CH stretch in the product formate anion, as detailed in the paper published in *J. Chem. Phys*.

Studies of Surface Adsorbate Electronic Structure and Femtochemistry at the Fundamental Length and Time Scales

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Funding:	$265,000

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 superatom states of hollow molecules such as fullerenes and aromatic molecules by low–temperature STM and electronic structure theory. The superatom states are interesting because they form nearly free electron bands holding the promise of metal-like charge transport in molecular systems. 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.

FY 2012 HIGHLIGHTS

We have been studying the transient exciton formation on Ag(111) surface. Upon two-photon resonant excitation from the occupied Shockley surface state to image potential state, we observe evidence of formation of an excitonic intermediate state in a three-photon photoemission process. This is interesting because metals, by definition, cannot support excitonic states. Our conclusion is that the exciton exists transiently because of the relatively slow screening of the Coulomb interaction in Ag. In order to study the exciton dynamics in greater detail, we developed a multi-dimensional, multiphoton photoemission technique. We measure the photoelectron energy and momentum distributions as a function of delay between the interferometrically scanned identical pump-probe pulses. By Fourier transforming the time axis, we obtain 2D electronic spectra as a function of parallel momentum of photoelectrons. These spectra help to reveal the coherent interactions that play a role in the transient exciton dynamics.

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

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Students:	1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$150,000

PROGRAM SCOPE

This project combines expertise from academe and national labs to advance the state of ab initio molecular dynamics (AIMD) simulation in handling hydrated ions in situations relevant for future research applications dealing with energy and the environment. To do so, community AIMD codes will be elaborated and augmented to incorporate new theoretical concepts and recent algorithmic advances, and to run more efficiently on the DOE leadership class computing platforms. This project complements the on-going experimental effort at the DOE labs to probe the microscopic structure of water solutions using advanced spectroscopic techniques. Building the capacity of predicting from basic quantum theory ionic processes and spectroscopic observations in solution is a grand-challenge for Materials and Chemical Sciences that will be addressed by our interdisciplinary team.

FY 2012 HIGHLIGHTS

This project started in September 2012, and to date progress is preliminary. However there are already several highlights. The Princeton team is completing a thorough analysis of ab-initio simulations of liquid water initiated in the context of the CMSN network on water and aqueous solutions led by the same group. Simulations of unprecedented accuracy have been performed including hybrid functionals, van der Waals interactions and nuclear quantum effects. The predicted water structures are in excellent agreement with recent x-ray and neutron experiments. Studies of water ions in solution performed in collaboration with the team members at Temple University are underway; these studies employ the new GW scheme developed at Princeton and show that the resulting electronic levels associated to the water ions are in excellent agreement with photoemission spectroscopy, greatly improving over earlier studies based on density functional theory. Finally, the development of a novel scheme for *ab-initio* molecular dynamics simulations of large systems consisting of more than 1,000 atoms is well underway at LBNL and at Princeton University.

CMSN: Structure and Dynamics of Water and Aqueous Solution in Materials Science

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Students:	3 Postdoctoral Fellow(s), 3 Graduate(s), 0 Undergraduate(s)
Funding:	$75,000

PROGRAM SCOPE

The goal of this project is to understand the structure and the spectroscopy (IR, optical, x-ray and neutron) of liquid water from *ab-initio* quantum mechanical theory. This grant partially supports research towards this goal at Princeton University, at UC Davis, and at the University of Washington. In addition, the grant stimulates debate and collaboration within a wider network comprising more than 30 theorists and experimentalists associated with other US universities, national laboratories, and major international research institutions. The program initiated with a kickoff workshop held at the Princeton Center for Theoretical Science on December 6-8, 2010. The second workshop of the series took place at the Talaris Conference Center in Seattle on February 10-12, 2012. A third workshop will be held at UC Davis in June 2013 at the end of the funding period.

FY 2012 HIGHLIGHTS

Research conducted at Princeton University showed that correlated proton tunneling occurs in the low temperature quantum phase transition from ice VIII to ice VII. Quantum correlation is signaled by the entanglement spectrum of the single particle density matrix associated to the protons.

In collaboration with experimental teams in Italy and the U.K., the Princeton group carried out an analysis of new deep inelastic neutron scattering probing the spherical momentum distribution of the protons in hexagonal ice. The study made use of new theoretical concepts introduced by the Princeton group in the previous funding period to extract the mean force experienced by the proton from the experimental Compton profile.

New calculations of the x-ray absorption spectra of liquid water under ambient conditions and of hexagonal ice close to melting were reported using a static GW approach developed by the group. This study found that including inhomogeneous effects in the screening and quantum disorder in the proton configurations was essential to bringing the theory in close agreement with experiment, so that the spectral differences between water and ice observed in experiments could be reproduced quantitatively in the calculations. This study indicated how the x-ray absorption and Raman scattering features reflect the changes in the H-bond network occurring upon melting/crystallization of water.

Interactions, Phase Equilibria and Self-Assembly in Ionic Systems

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Students:	1 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$225,000

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 and phase transitions of ionizable colloidal particles and pH-responsive polyelectrolyte thin films on flat and curved surfaces. For calculations of free energies of salt solutions, we use thermodynamic integration and staged insertions. Of particular interest is the temperature dependence of the activity and osmotic coefficients. 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 CO_2 geophysical sequestration applications, has not been previously determined. Our work in the area of ionizable polyelectrolyte films includes generation of morphology diagrams as a function of grafting density, surface curvature, solution pH and salt concentration, comparisons of our results with molecular mean-field theories, and elucidation of the differences in morphology and structure between dynamic (ionizable) models and fixed-charged models. For colloidal particles, interactions and phase transitions in the presence of salt are being studied and compared to those of fixed-charge asymmetric colloidal systems with central charges or a fixed pattern of charged groups of their surfaces. 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 2012 HIGHLIGHTS

Recent work in the group [Soft Matter, 8: 2385-2397 (2012)] has implemented long-range electrostatics within the HOOMD environment and obtained multiple long trajectories for coarse-grained models of ionic surfactants. The calculations established that previously accepted methods for determining the critical micelle concentration (cmc) are not accurate for strongly micellizing systems, and illustrated limitations in accuracy of the coarse-grained models. We have also developed a method for direct calculation of Donnan Equilibria, using a grand-canonical Monte Carlo scheme that properly accounts for the unequal partitioning of small ions on the two sides of a semipermeable membrane [Phys. Rev. E, 86: 016703 (2012)].

Optimizing New Materials for Solar Energy Conversion Via Quantum Mechanics

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Funding:	$144,000

PROGRAM SCOPE

This project employs a variety of computer simulation methods based on quantum mechanics to search for robust, inexpensive, and sufficiently efficient inorganic solid state materials that can form the basis for new photovoltaic or photoelectrochemical devices that convert sunlight to electricity. Various observables that are key metrics for determining the utility of a given material can be accurately calculated from quantum mechanics. These include the band gap (related to the built-in voltage), the absolute positions and character of the conduction and valence band edges (determines the relative energy and nature of the charge carriers), the electron-hole pair lifetime and recombination rate, and charge carrier mobility and conductivity. Limiting the design space to abundant elements and demanding robustness adds further constraints. As a result, we are focusing on first row transition metal oxide parent materials. The work is revealing which dopants or mixed oxides are likely to provide the most efficient solar energy conversion materials.

FY 2012 HIGHLIGHTS

MnO has high electron conductivity but absorbs very little sunlight due to its large band gap. DFT+U-led band gap engineering of MnO by alloying with ZnO suggests that a nanostructured 1:1 alloy will have a dramatically reduced band gap, moving from the ultraviolet down into the visible, as desired for improved sunlight absorption. The iron oxides, wustite (FeO) and hematite (Fe_2O_3), already absorb in visble, but they exhibit poor conductivity. Hole transport in pure and doped iron oxides was studied using embedded unrestricted Hartree-Fock (UHF) and complete active space self-consistent field (CASSCF) theories and the small polaron model. Holes in hematite are located on oxygen anions, whereas holes in wustite are located on iron cations due to the driving force toward half-filled d-shells on Fe. Wustite is naturally p-type due to intrinsic Fe cation vacancies. We predict that doping with hydrogen, lithium, or sodium may improve conductivity of wustiite by creating much shallower traps compared to those formed by vacancies. Among several dopants considered for hematite, the multivalent character of Mn doping facilitates local hole transport around Mn centers via a lowest-barrier O-Mn-O pathway. This suggests that higher hole mobility can be achieved with increasing Mn doping concentration, especially when a network of these low-barrier pathways is produced. DFT+U theory predicts that doping surface layers of hematite with cobalt or nickel provides optimal binding strengths for adsorbed intermediates that should reduce the overpotential of hematite photoanodes being explored for photoelectrochemical cells.

Towards Linear Scaling Electronic Structure via Partition Density Functional Theory, with Application to Electrochemical Capacitors

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PROGRAM SCOPE

The goal of this project is to explore a novel approach for the calculation of electronic properties of systems comprised of weakly-interacting fragments [partition density functional theory (PDFT)], overcoming fundamental limitations of standard electronic-structure methods. The more applied objective is to develop an efficient algorithm based on PDFT and apply it ultimately to determine the pore-size distributions that maximize the capacitance of nanoporous carbon materials used in electrochemical capacitors, a challenging task for *ab-initio* quantum chemistry.

FY 2012 HIGHLIGHTS

We completed a thorough investigation of the behavior of fragment occupations in PDFT, establishing conditions under which electronegativity equalization between fragments can or cannot be achieved. We formulated PDFT in terms of implicit functionals of the total density, and used the new formulation to propose an improved method for the calculation of partition potentials. We also extended the formalism to the spin-polarized case, and proposed a way to include external electric and magnetic fields. In parallel, we continued working on the implementation of PDFT into the NWChem quantum-chemistry code. The Wu-Yang algorithm was employed to obtain the partition potentials, and we carried out the first applications of PDFT to calculate the binding energies of diatomic molecules, from F_2 to I_2, reproducing standard DFT results while producing “partition energy” curves that can be used to suggest improved approximations for the partition energy functional (a central quantity in PDFT). This investigation allowed us to determine when and how to correct for basis-set superposition errors in the current implementation of PDFT. The results demonstrate that our algorithm works well with various functionals, and serve as a stepstone towards the larger goals indicated in the proposal.

Accurate Band Gaps for Tailor-Made Photovoltaic Materials

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PROGRAM SCOPE

The methodological development and computational implementation of novel symmetry projected methods for the accurate calculation of electronic excited states.

FY 2012 HIGHLIGHTS

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 make enforcing this orthogonality condition feasible. We are extending PQT and PHF to the study of excited states, even those with the same spatial and spin symmetries as the ground state. We will apply our techniques to such important problems as the spin-spin interactions in molecular magnets and photon absorption and conversion in dendrimers.

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

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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. Theoretical and experimental evidence suggests that asphaltenes are composed of aromatic molecules that contain 4-10 fused ring cores, with alkyl chain arms extending from the core. Sulfur and nitrogen are also present. Very little is known about the reaction pathways, combustion efficiency, and reactivity of these heteroaromatic species. We are currently characterizing the combustion and pyrolysis reaction channels available to asphaltene constituents such as thiophene and methyl thiophene.

FY 2012 HIGHLIGHTS

(1) Mechanistic Study of the 2-Thienylmethyl + HO_2 Radical Recombination Reaction: Radical recombination reactions are important in the combustion of fuel oils. Shale oil contains alkylated heteroaromatic species—the simplest example of which is the 2-thienylmethyl radical. The *ab initio* potential energy surface for the reaction of the 2-thienylmethyl radical with the HO_2 radical has been examined. Seventeen product channels corresponding to either addition/elimination or direct hydrogen abstraction have been characterized.

(2) Mechanisms for the Reaction of Thiophene and Methyl Thiophene with Singlet and Triplet Molecular Oxygen: Mechanisms on both the triplet and singlet potential energy surfaces have been investigated using *ab initio* methods. Geometries of various stationary points involved in the complex reaction routes are optimized at the MP2/6-311++G(d, p) level. The barriers and energies of reaction for all product channels were refined using single-point calculations at the G4MP2 level of theory. For thiophene, CCSD(T) single point energies were also determined for comparison with the G4MP2 energies.

Thiophene and 2-methylthiophene where shown to react with O_2 via two types of mechanisms, namely, direct hydrogen abstraction and addition/elimination. The barriers for reaction with triplet oxygen are all significantly large (i.e., > 30 kcal mol-1), indicating that the direct oxidation of thiophene by ground state oxygen might be important only in high temperature processes. Reaction of thiophene with singlet oxygen via a 2+4-cycloaddition leading to endoperoxides is the most favorable channel. Moreover, it was found that alkylation of the thiophene ring (i.e., methyl-substituted thiophenes) is capable of lowering the barrier height for the addition pathway. The implication of the current theoretical results may shed new light on the initiation mechanisms for combustion of asphaltenes.

Confinement, Interfaces, and Ions: Dynamics and Interactions in Water, Proton Transfer, and Room Temperature Ionic Liquid Systems

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PROGRAM SCOPE

Water exists in confined environments and at interfaces in a wide variety of important systems in chemistry, materials science, biology, geology, and technological applications. In chemistry, water plays an important role as a polar solvent often in contact with interfaces, for example, in ion exchange resin systems and chromatographic surfaces. Water in the nanoscopic channels of polyelectrolyte membranes is central to the operation of hydrogen and other fuel cells. In geology, interfacial water molecules can control ion adsorption and mineral dissolution. While a great deal is known about the dynamics of bulk water, much less is known about the dynamics of water in nanoconfinement at interfaces and when it is interacting with ionic species. The dynamics of water are changed a great deal when it is in nanoscopic environments, interacting with interfaces or ions.

A variety of nanoconfined water systems and interfaces, such as reverse micelles, lamellar structures, polyelectrolyte fuel cell membranes, and room temperature ionic liquids, are being investigated using ultrafast two-dimensional infrared (2D IR) vibrational echo techniques, and polarization and wavelength selective IR pump-probe experiments, as well as optical heterodyne detected optical Kerr effect (OHD-OKE) experiments and fast fluorescence. These methods permit molecular dynamics and intermolecular interactions to be studied in unprecedented detail. The 2D IR vibrational echo techniques are akin to 2D NMR, but they operate on time scales that are many orders of magnitude shorter than NMR. These ultrafast experiments are necessary to directly study the dynamical events on the time scales on which they occur. By combining direct measurements of the influence of nanoconfinement, interfaces, and charged species on water dynamics with observations of proton dynamics in the same systems, our understanding of proton transport is being substantially enhanced.

FY 2012 HIGHLIGHTS

We have used OHD-OKE experiments to study a series of room temperature ionic liquids (RTIL) with different alkyl chain lengths and containing a range of water concentrations. By looking over a vast range of times, we have determined that the nature of the molecular motions changes when water is added to RTILs with long alkyl chains. The data shows that water induces structural organization and orientational motions actually slow with additional water even though the viscosity decreases.

We have used 2D IR vibrational echo spectroscopy, IR pump-probe experiments, and OHD-OKE experiments to study mixtures of DMSO and water from very low water concentration to high water concentration. The experiments relate changes in structural organization to changes in the dynamics of both the water and the DMSO as the water concentration increases. We have also used 2D IR experiments to study the dynamics of surface functionalized with a heterogeneous catalyst. These are the first direct measurements of molecular surface dynamics.

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

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PROGRAM SCOPE

The goal of this project is to provide an accurate description of the structure and dynamics of the water molecules in the first shell of solvation of alkali metal ions with the ultimate objective of rationalizing selectivity in biological channels. Our strategy relies on *ab initio* molecular dynamics simulations based on state-of-the-art electronic structure calculations. Specifically, we aim at improving the accuracy of theoretical predictions based on DFT-GGA by introducing London dispersion forces into our equations of motion. To this end, we are using a novel approach based on a many-body treatment of vdW interactions to compute—on the fly—the appropriate corrections to DFT-GGA energies. A further improvement in accuracy will be subsequently achieved by using hybrid functionals that incorporate a portion of exact exchange from Hartree-Fock theory.

The development of the theory that introduces vdW corrections into DFT in a seamless fashion and the implementation of an efficient computational scheme to use hybrid functionals with a plane-waves basis set are currently in progress in the groups of collaborators Roberto Car at Princeton University and Xifan Wu at Temple University, respectively. Our first goal is to test the performance of this novel approach in predicting the structure of salt solutions containing Na^+ and K^+ ions. To this end, we are performing *ab initio* molecular dynamics simulations using three different GGA functionals (BLYP, HCTH, and PBE) and one hybrid (PBE0) exchange and correlation functional in combination with three different types of vdW correction (DFT+D, DFT+vdW-MB, and DFT+vdW-DF).

FY 2012 HIGHLIGHTS

The present program cycle started on September 1, 2012; therefore, the progress report for FY 2012 is relative to the one-month period between September 1, 2012 and September 30, 2012. Thus far, we compiled the Quantum-Espresso computational code on our local HPC resources and on NERSC-Hopper Cray XE6 and optimized our setup to get the best compromise between speedup and parallel efficiency. Furthermore, we started collecting trajectories and performed preliminary analyses. Results indicate a possible major role of dispersion interactions in determining the structure of the solvation shell of alkali metal ions. We observe also significant differences between our results and those reported in literature based on classical MD (e.g., CHARMM force field and polarizable models).

Density Functional Based Software for the X-Ray Based Spectra

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PROGRAM SCOPE

X-ray based core-hole spectroscopy (XPS, XAS (EXAFS and NEXAFS), XES) are important techniques for materials characterization. Through an 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 primary goal of this proposal is to develop a suite of software at various levels of sophistication to perform calculations of core-hole excitation spectra using first principles methods such as density functional theory. The software developed will include a robust suite of Perl/Python scripts to perform calculations on core-hole excitations of large systems on computers with large numbers of processors in parallel. A Graphical User Interface will be developed for visualization to identify the atoms of interest for core-hole calculations, to set up necessary inputs using pull up and pop-up menus, and for execution and analysis of the calculated spectra. These developments will allow users to obtain publication quality output of various spectra and may aid in interpreting results through visualization of molecular orbitals. The GUI development will bring the core-hole calculations to a level of user-friendliness so that it could also be used for classroom teaching of core-hole spectroscopy and molecular physics. Apart from software development, the 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. The core-hole spectroscopy is routinely used at various DOE supported laboratories and also in universities. The proposed developments and the resultant software will prove a very useful aid in analysis and interpretation of the experimental results.

FY 2012 HIGHLIGHTS

As a first step towards development of the software suite that will allow various core-hole excitation calculations on systems sizes of about 200 atoms, we started restructuring the code to eliminate the static allocations to alleviate memory demand for large systems. The majority of the code now uses dynamic allocations. Significant speed up in the diagonalization during the SCF step is obtained by implementing new algorithms for generalized eigenvalue problems from the linear algebra package. We also started GUI development using the device independent JAVA language. The current version of the GUI allows users to set up ground state calculations, visualize molecules under study, and submit calculations on local or remote machines. In the forthcoming year, these developments will be extended to the excited state calculations using perturbative delta SCF method.

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

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

PROGRAM SCOPE

The overall goal of the project is to develop density functional theory based algorithms that will provide a way to study the charge transfer process for a donor-acceptor molecular system. This development will provide a framework that can be systematically improved upon. In particular, our goal is to describe charge transfer excited states which are constrained to be orthogonal to the ground state and which can also be extended to describe the other excitations. Another goal is to simulate the effect of solvents on the charge transfer excited states in an approximate way and also to study the effect of the phonons. The goal is to ultimately develop a set of accurate and computationally efficient tools to predict the efficiency of a nanoscale photovoltaic. For that, one needs to be able to calculate the transition probabilities between various pairs of electronic, vibro-electronic, or vibonic states of interest. Depending on a given pair of states, the lowest-order transition rate may be dominated by solar-induced stimulated absorption, spontaneous recombination or cascade, vibrationally enhanced electron transfer, Förster processes, or Dexter processes. Determining these rates requires post-processing of accurate electron wavefunctions, the ability to rapidly determine electron-phonon interactions, and the role of polarization phenomena.

FY 2012 HIGHLIGHTS

We have applied a density functional theory based perturbative delta-SCF excited state method to a few donor-acceptor molecular systems, such as porphyrin-fullerene dyads, carotenoid-porphyrin-fullerene triad, and a multichromophoric heptad molecule, to study the charge transfer excited states of these systems. We have published an article on the accuracy of the excited state method by applying it to a benchmark set of small molecular conjugates. In another two articles on porphyrin-fullerene complexes, we studied the effects of various donors and acceptors and their orientations on the charge transfer states. The donor-acceptor components can have various orientations at the interface, depending on the experimental deposition parameters. We have also studied the CT states of a large multichromophoric hexad antenna connected to a fullerene acceptor. These studies establish the accuracy of the method for pure charge transfer states. Another study was pursued to determine the effect of morphology on charge transfer of a long floppy molecule containing a carotenoid, porphyrin, and fullerene. We studied the charge transfer states of a large number of structures that the molecule can adopt in a solution. We are also pursuing to incorporate the electrostatic effects of solvent molecules on the CT states using a QM/MM strategy. This work is being done for two different conjugates.

A Single-Molecule Approach for Understanding and Utilizing Surface and Subsurface Absorption to Control Chemical Reactivity and Selectivity

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Funding:	$137,000

PROGRAM SCOPE

Hydrogen adsorption, absorption, diffusion and reaction are key steps in a multitude of important energy related technologies from heterogeneous catalysts to hydrogen purification plants. Only recently has the true complexity of hydrogen's interactions with important catalytic metals like palladium become apparent with such realizations as the fact that subsurface hydrogen is often more catalytically active than surface hydrogen. Many important reactions have hydrogen dissociation and reaction at the center of their mechanisms. Therefore, for us to control and improve upon current hydrogen technologies, it is imperative to discover all we can about hydrogen's surface and subsurface chemistry and understand how it relates to each system's catalytic abilities. The project is aimed at quantifying hydrogen adsorption on and absorption in catalytically important palladium particles and alloys. This will allow us to explore the chemical reactivity and specificity of surface and subsurface hydrogen in a variety of industrially important hydrogenation reactions.

FY 2012 HIGHLIGHTS

Typical heterogeneous hydrogenation catalysts involve nanoparticles composed of expensive noble metals or alloys based on platinum, palladium, rhodium, and ruthenium. We demonstrated for the first time how single palladium atoms can convert the otherwise catalytically inert surface of an inexpensive metal into an ultra-selective catalyst. We used high resolution imaging to characterize the active sites in our single atom alloy surfaces, and we used temperature programmed reaction spectroscopy to probe the chemistry. The mechanism involves facile dissociation of molecular hydrogen at individual palladium atoms followed by spillover onto the copper surface, where ultra-selective catalysis occurs by virtue of weak binding. Interestingly, some of the best industrial alloy catalysts to date may already be operating via this mechanism, but there is currently no way to directly probe the atomic geometry of an alloyed nanoparticle of a working catalyst. Through surface science experimentation we were able to unambiguously show how beneficial a fully atomic dispersion of an active element can be and we pose a challenge to the catalysis community to synthesize similar ensembles in real catalysts.

Exploring the Random Phase Approximation for Materials Chemistry and Physics

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

PROGRAM SCOPE

This project is an exploration of the random-phase approximation (RPA) or RPA-like methods for first-principles electronic-structure calculations for atoms, molecules, solids, surfaces, and nano-structures. The applications in this proposal are challenges for the simpler approximations of Kohn-Sham density functional theory, which are part of the current “standard model” for quantum chemistry and condensed matter physics. On the other hand, these applications can also lead to a better understanding of shortcomings of the RPA method.

Direct RPA includes the full exact exchange energy and a nonlocal correlation energy from the occupied and unoccupied Kohn-Sham orbitals and orbital energies, with an approximate but universal description of long-range van der Waals attraction. The RPA has a correct long-range correlation. However its short-range correlation hole is too deep, leading to errors in the total energy that cancel out of solid-state energy differences better than they cancel out molecular energy differences. Our applications cover (1) carbon monoxide and hydrogen adsorbed on transition-metal surfaces where the RPA method has not been tested yet; (2) carbon dioxide adsorption on surfaces to reduce the green-house effect; (3) the lattice constants, spin moments, and band gaps of strongly-correlated transition-metal oxides; and (4) structural phase transitions under pressure in solid Si, SiO_2, Zr, and Ca. A nonempirical, spatially nonlocal, frequency-dependent model for the exchange-correlation kernel will be developed and tested for use in the adiabatic-connection fluctuation-dissipation theorem, as a correction to direct RPA.

FY 2012 HIGHLIGHTS

From the start date of the project in July 2012, our efforts mainly focused on understanding the effects governing structural phase transitions in solids. We performed RPA calculations on Si crystals and established that RPA overall performs better than semilocal density functionals. This work was just published in PRB: B. Xiao, J. Sun, A. Ruzsinszky, J. Feng, and J.P. Perdew, Structural Phase Transitions in Si and SiO_2 Crystals via the Random Phase Approximation, *Physical Review B* 2012, 86, 094109.

Phase transitions can be more complex if they occur in strongly-correlated systems, like VO_2. Currently we are computing structural phase transitions in this system and comparing the performance of the RPA to standard density functional approximations.

Parallel to the structural phase transitions, we are applying the RPA to surface adsorption problems. The RPA has been successfully applied to the adsorption of the CO molecule on a Pd surface. However, it does not seem to bind the CO molecule on an Ag surface. We are currently working to understand this problem.

Model Catalysts by Size-Selected Cluster Deposition

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Funding:	$160,000

PROGRAM SCOPE

The goal of our research is to explore correlations between supported cluster size, electronic and morphological structure, the distributions of reactant binding sites, and catalytic activity, for model catalysts prepared using size-selected metal cluster deposition. This focus is motivated, in part, by a discovery a few years ago of a very strong correlation between metal core-level binding energies and catalytic activity for CO oxidation. The work to date has focused on catalysts with catalytically active metal clusters deposited on metal oxide supports, and on electrocatalysis by metal clusters on glassy carbon electrodes. We are also looking at effects of cluster size on Pd-catalyzed H_2 splitting and uptake in metals.

FY 2012 HIGHLIGHTS

We carried out a study of electrocatalysis by size-selected Pt clusters deposited on glassy carbon electrodes. The intention was to examine activity for oxygen reduction (ORR) as a function of cluster size; however, we discovered something even more interesting. We found that all but a few of the Pt_n ($n \leq 11$) were highly efficient oxidation catalysts, catalyzing electrochemical oxidation of the glassy carbon by water: $C(s) + 2\ H_2O \rightarrow CO_2 + 4\ H^+ + 4\ e^-$. The cycle is completed by reduction of H^+ to H_2 at the counter electrode, resulting in the net reaction: $C(s) + 2\ H_2O \rightarrow CO_2 + 2\ H_2$. Current densities of up to 1 A/cm^2 were observed. The exception to this behavior was Pt_7, which was found to behave “normally”, i.e., catalyzing ORR in the appropriate potential ranges, with mass activity similar to that of conventional catalysts with Pt nanoparticles on glassy carbon. In addition, Pt_{10} and Pt_{11} behaved in an intermediate fashion, showing ORR activity, but also some propensity for carbon oxidation. From a fundamental perspective, the most interesting observation here was that the activity for carbon oxidation showed a one-to-one correlation with the Pt 4f orbital binding energy, measured by photoemission. The result is also interesting for practical reasons. Carbon oxidation by water, catalyzed by Pt, corrodes fuel cell electrodes. Our results, where carbon oxidation was very efficient for small Pt clusters, but not observed significantly for larger nanoparticle-containing catalysts, suggests that the dominant "problem" species may be very small Pt clusters present on the fuel cell electrodes. Potentially, the very high activity of these small Pt clusters as oxidation catalysts could also be important for H_2 generation or as a compact electrochemical source.

In addition, experiments on CO oxidation catalyzed by Pd_n/alumina have been carried out, looking for correlations with both UV and X-ray photoemission energies. We are currently examining the effects of alumina film thickness on both the size-dependent activity and the physical properties of the clusters.

Spectroscopy of Organometallic Radicals

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PROGRAM SCOPE

In this project, we measure electronic spectra of small organometallic radicals with the goal of elucidating the chemical bonding and electronic structure of these unsaturated species, which are representative of transient intermediates in homogeneous and heterogenenous catalysis. We seek to obtain accurate information that can be used to calibrate quantum chemical calculations on these complicated species. We are also working on small molecules containing thorium or uranium, where the presence of low-lying or partially occupied 5*f* orbitals introduces additional complexity. For the small actinide molecules, almost no detailed gas-phase spectroscopic data is available, except for a very few species. Neutral molecules are studied using pulsed laser ablation of a metal disk in the throat of a pulsed supersonic expansion of helium seeded with reactant gases. The molecular beam is then subjected to tunable pulsed dye laser radiation, followed by an ionization laser pulse of a suitable wavelength. Any photoions formed are detected in a time-of-flight mass spectrometer. The optical spectrum is obtained by scanning the dye laser and recording the ion signal as a function of dye laser wavenumber. The spectra provide bond lengths, electronic state symmetries, and vibrational frequencies, and may be directly compared to computational results.

In a new instrument that is currently under construction, mass-selected cations will be spectroscopically investigated by trapping them in a cryo-cooled 22-pole radio frequency trap and irradiating them with pulsed dye laser radiation. If the molecule absorbs the radiation and photodissociates, fragment ions will be detected, allowing the optical spectrum to be recorded by monitoring fragment ion signal as a function of laser wavelength.

FY 2012 HIGHLIGHTS

We have resolved the rotational structure in electronic spectra of CuCCH, allowing us to identify two excited electronic states. The ground state is a closed-shell $^1\Sigma^+$ state, which undergoes a spin-forbidden transition to an excited state of either $^3\Pi_1$ or $^3\Sigma_1$ symmetry near 20249 cm^{-1}. A second electronic band system is also observed showing that an excited $^1\Sigma^+$ state lies near 23130 cm^{-1}. A third excited electronic state near 24663 cm^{-1} has not been rotationally resolved, but is likely of $^1\Pi$ symmetry.

In work on diatomic UN, a complicated electronic spectrum has been recorded that shows a large number of excited electronic states. Several bands have been rotationally resolved, providing a ground state bond length of 1.764 Å. The ground electronic state has an angular momentum along the internuclear axis of $\Omega''=3.5$. This probably results from a $U^{3+}N^{3-}$ structure, in which the U^{3+} ion is in its $5f^27s^1$, $^4H_{3.5}$ level, which is split in the presence of N^{3-}, resulting in a ground level of UN that derives from the $5f\phi^15f\delta^17s\sigma^1$, $^4H_{3.5}$ term.

Hydration Mechanisms in Nanoparticle Interaction and Surface Energetics

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Funding:	$121,000

PROGRAM SCOPE

Emerging nanoparticle technologies require new techniques to control surface properties of a material. Surface thermodynamics and interactions between nanoparticle surfaces are often 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 focus is 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 external electric field. The project relies on a combination of theory and simulation techniques 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 anticipates to uncover 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.

FY 2012 HIGHLIGHTS

Our analysis and molecular modeling enabled thermodynamic predictions for wetting of chemically or topologically patterned surfaces and uncovered a new mechanism of nanodroplet stabilization associated with surface heterogeneities. We determined the relation between the wetting free energy and the extent of ionic functionalization and provided a comparison with the effect of commensurate electrode charge. Our findings provide guidance for the design of ionically nanopatterned materials with tailored hydrophilicity at preserved material structure and minimal chemical modification, as illustrated on the example of alkyl- and ionic-functionalized graphane surfaces wetted by salt solution. Future studies concern nanopore wetting and dewetting by saline solutions under applied field to enable flow regulation and surface-energy conversion in porous media under electric control.

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

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Funding:	$132,000

PROGRAM SCOPE

The main objectives are to develop a comprehensive program starting from electronic structure and magnetic properties of free clusters for identifying stable magnetic motifs of varying band gaps, investigate the transport properties of molecules of such motifs, and then explore synthesis and properties of larger assemblies of such units. The program involves four interrelated areas of study: (1) extending our recent finding of magnetic superatoms to a wider class of clusters including 3D and 4D transition metal atoms and their clusters, coated with alkali, alkaline earth, Ag, and Au atoms; (2) studying ligated clusters containing transition metal atoms and clusters coated with thiolate and other ligands; (3) studying silicon transition metal clusters to find stable magnetic motifs containing multiple transition metal and silicon atoms; and (4) developing and using computational codes to carry out electronic transport studies that incorporate the effect of excess charge, spin ordering, and easy axis. Thereafter, building on our recent successes in synthesizing nanoassemblies using synthetic chemical methods, we plan to collaborate with experimental groups to verify the predictions of stable building blocks and synthesize assemblies of such units. A long-term objective is to develop guiding principles that can direct a systematic search of new building motifs that could lead to materials with tunable characteristics.

FY 2012 HIGHLIGHTS

We have examined the stability and magnetic properties of $TMSr_n$ and $TMCa_n$ clusters containing transition metal atoms surrounded by multiple Sr and Ca atoms to search for magnetic superatoms ideal for developing molecular units. Our studies show that a $FeCa_8$ cluster with a magnetic moment of 4 bohr magneton and $MnSr_8$ with a magnetic moment of 5 bohr magneton are highly stable species with exchange splitting of 0.61 and 1.82 eV, respectively. Both clusters maintain their identity as combined to form superatomic molecular units indicating viable units for molecular transport. To demonstrate the novel features offered by such units, we examined the transport through a superatom dimer (Cs_8V)-(Cs_8V) using density functional theory combined with nonequilibrium Green's-function formalism. The findings indicate that the transport is sensitive to the binding site and the contact distance between the dimer and the electrode, and that the equilibrium conductance exhibits an oscillatory behavior with the contact distance. The equilibrium conductance in ferromagnetic state shows an unusually high spin polarization that exceeds 80% at large contact distances and the I-V curve shows negative differential resistance for specific contact distance, whose origin lies in the variation of the coupling between the superatom and the electrode with external bias.

Correlating Electronic and Nuclear Motions during Photoinduced Charge Transfer Processes using Multidimensional Femtosecond Spectroscopies and Ultrafast X-ray Absorption Spectroscopy

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

PROGRAM SCOPE

The goal of this research program is to measure coupled electronic and nuclear motions during photoinduced charge transfer processes in transition metal complexes by developing and using novel femtosecond spectroscopies. In this program, we will use a unique two-pronged experimental approach to relate commonly measured kinetic parameters in transient photochemical experiments to the time-evolving distributions of molecular and electronic structures of the reactants and products and their interactions with the solvent bath. One part of the research program will focus on the development of novel three-dimensional visible-infrared experiments employing a sequence of visible and infrared fields to directly correlate electronic and vibrational motion during ultrafast photochemical reactions. These experiments will measure time-dependent anharmonic vibrational couplings of the high-frequency solute vibrations with the low-frequency solvent and solute degrees of freedom, time-dependent vibronic couplings, and elucidate the role of incoherent and coherent vibrational relaxation and transfer pathways during and following electron transfer. The second thrust of the program involves using and developing transient x-ray absorption spectroscopy (XAS) to understand changes in the electronic structure of molecules following light absorption.

FY 2012 HIGHLIGHTS

We have performed a fifth-order nonlinear experiment to directly measure time-dependent intramolecular vibrational dynamics among a system of highly coupled high frequency stretching modes indirectly populated by ultrafast back electron transfer. We have applied transient Ru L-edge XAS to study the rearrangement of electron density following photoexcitation of a widely used solar cell dye molecule. Our experiment shows that the initial charge transfer excitation modifies the electronic structure on the thiocyanate ligands and could provide a driving force for the regeneration process explaining the superior efficiency of the dye in devices.

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

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PROGRAM SCOPE

Developing and applying accurate, yet computationally inexpensive, quantum electronic dynamics methods for understanding fundamental chemical physics is the focus of our work. We have demonstrated that the real-time time-dependent density functional theory (TDDFT) implemented within a non-adiabatic Ehrenfest dynamics technique is a very powerful tool to obtain insight into electronic dynamics that is beyond the ground state framework. We focus on developments and applications of a first-principles electron friction method and open-system framework that can give rise to correct chemical kinetics of wave function decoherence and energy dissipation, completely described within electronic structure TDDFT theory. With such a computational workhorse and development plans to expand the ability and utility of the TDDFT electronic dynamics, we are in a great position to explore many exciting and complex phenomena: laser-controlled molecular reactions, lifetimes of excited states on surfaces, interfacial charge transfer dynamics, surface-enhanced chemical processes, and excitonic dynamics in nanocrystallines. The TDDFT electronic dynamics will have a broad impact in designing materials and reactions for new opto-electronics, electro-optics, and more efficient and environmentally friendly catalysts.

FY 2012 HIGHLIGHTS

We have derived and developed a method to describe the dynamical interactions between excited state electronic dynamics and a polarizable continuum solvation bath within the open-system framework. Solvent electronic degrees of freedom are coupled to the time-dependent electronic density of a solute molecule by means of the implicit reaction field method, and the entire electronic system is propagated in time. This real-time time-dependent approach, incorporating the polarizable continuum solvation model, is shown to be very effective in describing the dynamical solvation effect in charge transfer process and yields consistent absorption spectrum in comparison to the conventional linear response results in solution. In addition, this method provides insights into how solvent modulates solute excited state dynamics.

Computational Design of Metal Organic Frameworks for Photocatalytic Reduction of CO_2

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Funding: $115,000

PROGRAM SCOPE

This is a joint project with Professor J. Karl Johnson in the Department of Chemical and Petroleum Engineering at the University of Pittsburgh. The main objective of this project is to explore new porous coordinated polymer materials that exhibit photoactive properties. Such materials will yield a number of benefits where the absorbed sunlight can be used in the PCP framework to perform a desired effect. For example, we are currently exploring PCPs that will reduce CO_2 utilizing sunlight energy from a photocatalytic PCP material. As part of this combined project, our research group is focusing on developing non-adiabatic molecular dynamics simulation tools within FIREBALL (a local orbital-based density functional theory method) so that we can understand the charge excitation dynamics in photoactive PCP materials. Additionally, we are working with Johnson to understand some catalytic properties of published PCPs; we are using umbrella sampling (molecular dynamics) within FIREBALL to obtain the free energy barriers associated with a chosen reaction coordinate. Our research is strongly coupled with two chemical synthesis research groups (Christopher Matranga at the National Energy Technology Laboratory and Professor Hongcai Zhou at Texas A&M University) so that we are pursuing materials that are directly relevant to their synthesis and characterization.

FY 2012 HIGHLIGHTS

In collaboration with Professor Oleg Prezhdo in the Department of Chemistry at the University of Rochester, we have developed and implemented state-of-the-art non-adiabatic molecular dynamics (NAMD) algorithms in our FIREBALL code. The results of this implementation and application to a variety of molecules, including azobenzene (important for azobenzene functional PCPs synthesized by Zhou), is the topic of a manuscript submitted to the *J. Phys. Chem. C.* Furthermore, we have utilized our NAMD method to examine ensembles of the *cis* to *trans* conformational change in stilbene, where we choose several hundred initial configurations. The resulting properties of these simulations are then plotted as distributions for determining the probabilistic outcome of events. The interesting note to make is that simulating single or few events does not correctly model the excitation dynamics or the outcome; the outcome is a probability event and ensemble calculations yield correct physical and chemical insight.

We have also studied reactions in a porphyrin PCP that has been experimentally studied by Hupp and coworkers. The Mn-porphryin PCP, which Hupp et al. studied, is one of a very few PCPs shown to have high catalytic activity. With co-PI Johnson, we have utilized umbrella sampling to explore the reaction processes for styrene oxidation within this material and we are exploring the reaction pathways and free-energy barrier heights.

Quantum Monte Carlo Calculations of Chemical Binding and Reactions

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PROGRAM SCOPE

The goal of this project is to apply auxiliary field quantum Monte Carlo (AFQMC) to reliably predict binding strengths and reaction pathways in systems important to energy management. With Gaussian type orbital (GTO) basis sets, AFQMC treats the same Hamiltonian as that of corresponding quantum chemistry many-body calculations. We have shown that compared to coupled-cluster CCSD(T), the preeminent many-body quantum chemistry method, the accuracy of the phaseless AFQMC is similar near equilibrium geometries and better when bonds are stretched. Because AFQMC exhibits much better size scaling than standard quantum chemistry approaches, it provides new opportunities for efficient and accurate many-body calculations of ground and excited states.

FY 2012 HIGHLIGHTS

We have recently implemented the frozen-core (FC) approximation into AFQMC with GTOs. This reduces the number of correlated electrons that must be treated, resulting in greatly improved efficiency, without having to rely on pseudopotentials. The FC-AFQMC method was applied to study the functionalization of graphene with cobalt adatoms to induce localized magnetic moments in graphene. To date, calculations of Co/graphene systems have largely been done at the density functional theory level with local or semi-local functionals. However, the applicability of methods based on independent-electron approximations in such systems is unclear since electron correlation effects can be significant. Indeed, widely varying results have been reported for the nature of the magnetic state and binding of Co as a function of adsorption height. We found that as a function of the distance *h* between the Co atom and the six-fold hollow site, there are three distinct ground states corresponding to three electronic configurations of the Co atom. Two of these states provide binding and exhibit a double-well feature with nearly equal binding energy of about 0.4 eV at h ~ 1.51 and h ~ 1.65 Angstroms, corresponding to low-spin and high-spin Co configurations, respectively. Gating such a system could induce switching between the two magnetic states, which may have potential for use in spintronic devices.

Enabling High-Throughput Computational Screenings of Nano-Porous Materials via Transferable, Physically-Motivated Force Fields and Novel Simulation Methodologies

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Funding:	$240,000

PROGRAM SCOPE

The research objectives of this work are to develop the theoretical framework necessary to generate transferable and physically-motivated classical force fields for complex systems and to apply these methodologies to the specific case of gas adsorption in nanoporous metal-organic framework systems.

FY 2012 HIGHLIGHTS

We have made a number of significant advances towards our larger goal of enabling high-throughput screening of nano-porous materials for adsorption/separation processes. (1) We recently developed a robust, *ab initio* approach for generating physically-motivated force fields from symmetry-adapted perturbation theory. Over the last year, we generalized this approach to yield transferable force field parameters for a wide range of functionalized metal-organic frameworks (MOFs), yielding semi-quantitative to quantitative agreement with experimental results (where available), without any empirical or experimental input. Although we have used this approach almost exclusively for developing force fields for nano-porous materials, the idea is general and could be applied to generic condensed phase simulations. (2) We also developed a rigorous, hierarchical lattice model approach for screening adsorption and transport properties in nano-porous materials. Our approach derives an efficient lattice model from an underlying atomistic one using a rigorous statistical mechanical approach, exact in the low density limit and accurate up through saturation. Crucially, this enables screening and full isotherm calculations two to three orders of magnitude more quickly than from conventional atomistic simulations. The resulting lattice model can also be used to rapidly estimate transport properties via calibration against atomistic simulations. (3) Finally, we examined the impact of ubiquitous flue gas contaminants (SO_x, NO_x and hydrates thereof) on coordinatively unsaturated MOFs containing “open metal” sites. We find that, in spite of their small (ppm) concentrations, these contaminants bind extremely strongly to the open metal sites and effectively out-compete CO_2 under equilibrium conditions, despite the former’s small concentration. Our work highlights that these contaminants are an important consideration with respect to MOFs under realistic flue gas conditions.

Water Dynamics in Heterogeneous and Confined Environments: Salt Solutions, Reverse Micelles, and Lipid Multi-Bilayers

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Funding:	$120,000

PROGRAM SCOPE

Our goal is to understand the structure and dynamics of water in its different phases, at the interfaces between these phases, and in confined and heterogeneous environments. To this end, linear and nonlinear vibrational spectroscopy is playing a very important role. We are developing techniques for calculating spectroscopic observables and using our results to analyze and interpret the experiment.

FY 2012 HIGHLIGHTS

We have found the dynamics of water in the interior of reverse micelles is much slower than that of bulk water and depends on curvature of the interface. The dynamics of water between lipid bilayer membranes is also very slow, and rotational relaxation is very non-exponential.

The Role of Electronic Excitations on Chemical Reaction Dynamics at Metal, Semiconductor, and Nanoparticle Surfaces

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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 2012 HIGHLIGHTS

We made three distinct accomplishments. First, in collaboration with the experimental group headed by Alec Wodtke of the Max Planck Institute in Göttingen, we applied our Independent Electron Surface Hopping (IESH) simulations of nitric oxide scattering from a gold surface to compute vibrational excitation probabilities. Using the same intermolecular interactions developed for the previous studies of vibrational de-excitation, we obtained good agreement with the new experimental results on excitation over a wide range of incident energies and surface temperatures. Second, we introduced electronic and phonon energy dissipation into IESH to more realistically describe transfer of energy between the explicitly simulated local region of the surface and the bulk substrate. Initial applications to vibrational lifetimes and laser-induced desorption appear promising. Third, we carried out a theoretical analysis of the asymmetric vibrational lineshapes in water cluster anions, as observed by the experimental group headed by Mark Johnson of Yale University, revealing the competition between outgoing electron channels that determines the asymmetry.

Critical Evaluation of Theoretical Models for Aqueous Chemistry and CO_2 Activation in the Temperature-Controlled Cluster Regime

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Funding:	$205,000

PROGRAM SCOPE

Our joint program integrates experimental and theoretical methods to exploit the unique properties of isolated cluster ions as media in which to quantify the molecular-level interactions underlying the cooperative behavior of solvent networks such as that found in liquid water. This involves determining the structures of neutral and charged water clusters, both as a homogeneous solvent and embedded with solutes corresponding to labile intermediates in radiation-damaged systems. The goal is to provide benchmarks that calibrate both density functional and ab initio methods, as well as model approaches that can handle larger systems and longer time scales. The measurements are carried out using custom instrumentation involving freezing out local minima with Ar-mediated cluster synthesis and structurally characterizing them through theoretical analysis of their vibrational predissociation spectra. We have recently dramatically expanded the chemical scope of our “bottom-up” approach by integrating a temperature-controlled ion processing capability that can sample complex molecules directly from solution using electrospray and other ionization schemes. An example of the information that can be obtained with our approach is our identification of the structural motifs that water networks adopt in order to accommodate this excess electron. Another on-going focus is to understand the underlying mechanics of water behavior that is obscured in measurements on the macroscopic system. Our approach involves monitoring the temperature-dependent spectral diffusion of isotopically labeled water clusters. A new direction for our efforts involves addressing the interesting properties of ionic liquids that are responsible for their role as solvents for the catalytic activation of CO_2.

FY 2012 HIGHLIGHTS

We unraveled the molecular-scale mechanics of solvent-mediated electron scavenging. This was achieved using Ar-assisted condensation to trap a neutral CO_2 molecule on a negatively charged water cluster to prepare the $CO_2\cdot(H_2O)_6^-\cdot Ar$, “entrance channel” complex of the elementary reduction reaction. Infrared vibrational excitation of this meta-stable assembly then triggered the water network deformations, leading to formation of the microhydrated CO_2^- radical anion. Molecular dynamics simulations of this reaction then elucidated the specific network rearrangements that lead to eduction of the CO_2. These results were published as a cover article in *J. Phys. Chem. A*. Another completed project involved elucidation of the microscopic mechanics of excess electron attachment to the multiple H-bond bridge at the heart of radiation-induced DNA damage. This was accomplished using the formic acid dimer anion, $(HCOOH)_2^-$, as a model system where we could follow the intracluster, electron induced proton transfer event. The spectroscopic signature of the proton-transferred species was rationalized based on the anomalous solvatochromic response of the CH stretch in the product formate anion, as detailed in the paper published in *J. Chem. Phys*.

DOE National Laboratories

Multi-Scale Modeling of Energy-Related Phenomena

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PROGRAM SCOPE

The primary focus of this research is on the development and application of theoretical and computational methods that enable the study of surface phenomena, heterogeneous catalysis, surface and bulk properties of solid clusters, properties of liquid clusters and their formation and reactions, solvent effects, and mechanisms in organometallic chemistry including solvent and relativistic effects. It is an integrated effort including both electronic structure theory and non-equilibrium statistical mechanical and multiscale modeling.

Our electronic structure theory efforts integrate the development of fundamental theory with optimal strategies for computational implementation within GAMESS, a freely distributed *ab initio* quantum chemistry package, and NWChem, an open source program for large scale molecular simulations. This research expands the capability for accurate treatment of large or complex systems of interest to DOE. In particular, this includes development of embedding methods, effective fragment potential approaches (with special interest in liquid-solid interfaces) and a rigorous basis for semi-empirical tight-binding methods, all geared towards applications to various complex condensed phase systems. A new effort is focused on excited state electronic structure and non-adiabatic dynamics with applications to catalytic systems.

Our statistical mechanical & multiscale modeling component involves studies of surface phenomena that are typically integrated with relevant electronic structure analyses. A core focus in this effort is the modeling of chemisorption and heterogeneous catalysis on transition metal surfaces. We consider both reactions on extended surfaces (including multi scale studies of spatiotemporal behavior) and in nanoscale catalyst systems (including analysis of fluctuation effects). We also model transport and reaction processes at non-conducting surfaces and in mesoporous systems, and analyze fundamental behavior in general far-from-equilibrium reaction-diffusion systems.

FY 2012 HIGHLIGHTS

Ab initio electronic structure calculations were performed to develop an understanding of the adsorption energetics and diffusion of Ga and Ga_2 on the Si(100)-2×1 reconstructed surface. These processes were modeled with a QM ($Si_{15}H_{16}$) and a larger QM/MM ($Si_{199}H_{92}$) molecular cluster. The MRMP2//CASSCF relative energies from the QM/MM model indicate that the on-dimer site is the global minimum on the potential energy surface. An important consideration in developing an understanding of the relative energies of various species on the Si(100) surface is the trade-off between metal-surface bonding vs. metal-metal bonding. In order to form metal rows, metal atoms must give up some of their bonding to the surface in order to achieve stronger metal-metal bonding. Importantly, QM-only and QM/MM geometries have noticeable differences because the QM cluster does not have sufficient structural rigidity. So, it is essential to use clusters of adequate sizes to model surface phenomena. This work was reported in L. Roskop, J.W. Evans, and M.S. Gordon, J. Phys. Chem. C, 115, 23488 (2011).

Theoretical and Computational Tools for Modeling of Energy-Relevant Catalysis

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PROGRAM SCOPE

The goal of this research is to advance multi-scale modeling of catalytic processes related to energy needs. The DOE/BES Basic Research Needs Report on Catalysis for Energy Applications identified two coupled Grand Challenges: (1) understanding reaction mechanisms and dynamics, and (2) designing and synthesizing catalyst structures. Addressing these challenges with novel approaches is essential for the effective and efficient production of fuels. The report noted the critical role of theory, computation, and simulation in providing the molecular-level understanding necessary to address these challenges.

Regarding the first Challenge, advances in highly-scalable high-level electronic structure methods, including novel hybrid multi-level approaches, are critical to elucidating reaction mechanisms and dynamics in complex environments. Also, describing the overall catalytic reaction process on the meso- or macro-scale requires coupling to either traditional microkinetic modeling or, preferably, to molecular-level statistical mechanical modeling. Regarding the second Challenge, there is a need for high-level modeling of the non-equilibrium formation kinetics and structure of catalyst (nano)materials. Our research explores the development of separate and integrated combinations of electronic structure analysis, reactive force-field methodologies, and statistical mechanical and coarse-grained modeling approaches. These efforts incorporate the development of novel approaches in not only theoretical chemistry and materials science (BES), but also computational science and applied mathematics (ASCR).

The targeted catalytic materials include mesoporous oxide surfaces as well as metal surfaces and supported nanostructures. Of particular interest is energy-relevant catalytic reaction processes utilizing mesoporous silica nanoparticles, and reactions catalyzed by metal surfaces and nanoclusters. For the description of both reaction kinetics and catalyst structure, electronic structure and reactive force-field calculations provide input for the statistical mechanical and coarse-grained modeling.

FY 2012 HIGHLIGHTS

Efforts continued utilizing reactive force-field and higher-level methods to characterize conformations and relative energies of covalently-bound functional groups within the pores of mesoporous silica. Results were compared with those from NMR studies by the Homogeneous and Interfacial Catalysis in 3-D Controlled Environments program at Ames Laboratory. In another parallel effort, we have developed coarse-grained spatially-discrete stochastic models to describe the interplay between restricted transport and catalytic conversion reaction kinetics in these nanoporous systems. A key accomplishment was the development of a novel formalism capturing both the anomalous nature of transport in narrow pores and the critical effects of fluctuations in the adsorption/desorption of reactants and products at the pore openings [Ackerman *et al.*, Phys. Rev. Letters, 108 (2012) 228301]. This formalism succeeds where previous approaches have failed. It provides an effective and efficient theoretical tool to explore the variation of reactivity within a large phase-space of experimental parameters (describing both the catalytic material and the reaction process), thereby guiding the experimental optimization of catalytic systems.

Single Molecule Chemical Imaging at Femtosecond Time Scales

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Funding:	$558,000

PROGRAM SCOPE

We propose to develop and exploit an advanced experimental approach that integrates ultra-high vacuum (UHV) scanning tunneling microscopy and spectroscopy and single particle laser spectroscopy in order to explore the photophysics of single molecules or molecular complexes with atomic-scale spatial resolution and ultrafast time scales. The overarching 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 goal is critical to connecting with theoretical efforts to develop a deeper understanding of photophysics in these systems, which are at the heart of photovoltaic, photocatalytic, and photosynthetic processes. We will explore photo-induced charge-separation and conformational changes in bio-inspired photosynthetic complexes and acceptor-donor molecular complexes.

Additionally, we will also study the local photo-excited properties of small molecule acceptor-donor complexes that will be constructed though self-assembly on surfaces in UHV. Our approach will also include developing new graphene-encapsulated plasmonically active substrates in order to facilitate improved tip-enhanced Raman studies of these molecular systems. The work will be performed in close collaboration with experimental and theoretical colleagues at Northwestern University.

Theoretical/Computational Studies of the Fundamentals of One-Component and Alloy Metal Based Nanocatalysis Relevant to Alternative Sources of Energy

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PROGRAM SCOPE

The goal of this project is to execute a program of theoretical/computational studies directed at advancing our fundamental understanding, characterization, and utilization of novel one-component and alloy metal nanocatalysts relevant to alternative sources of energy and new chemistries. The emphasis is on unraveling and characterizing the separate and combined roles of structural and electronic effects in defining the functionalities of these nanocatalysts and the key mechanisms that underlie their activity and selectivity. These are investigated as a function of the catalytic particles' size and composition, as well as the possible role of ligand modifiers. Among the primary targets are catalysts and reactions relevant to new sources of energy, e.g., glycerol reforming into hydrogen, production of green oxidants such as hydrogen peroxide, selective hydrogenation of unsaturated hydrocarbons, e.g., alkynes into alkenes, and others. Our theoretical/computational studies are carried out in close contact with ongoing related experimental programs at Argonne. We aim not only at rationalizing and explaining data obtained in measurements, but also at assisting and guiding future experiments. The emphasis is on fundamental scientific issues and knowledge/understanding that are critical for making the next empowering qualitative leap in advancement of the broad field of catalysis and the various technologies related to it.

FY 2012 HIGHLIGHTS

One aspect of our density functional theory based studies involved comparative characterization of structural, electronic, and chemical reactivity properties of pure Pt and Mo, and mixed Pt/Mo nanocatalysts. The properties computed and analyzed include the stability of the catalysts as a function of their size and composition, as well as adsorption and transition state conformations and energetics for their reactions with CO, glycerol, and fragments of glycerol relevant to its reforming. Among other things, our computations revealed that admixing Mo to Pt nanocatalysts lowers the binding energy of CO to Pt sites, which results in mitigation or even alleviation of the well-known CO poisoning problem. Another aspect of our work explored structural, electronic, and chemical reactivity properties of Pd nanocatalysts. In particular, we characterized different adsorption and transition state conformations and energetics for molecular and dissociative adsorption of H_2 and O_2 on these nanocatalysts. The information gained is relevant to direct production of hydrogen peroxide from hydrogen and oxygen using Pd as a catalyst. Yet another component of our studies clarified the role of capping ligands such as amines in regulating the selectivity of Pt nanocatalysts towards partial hydrogenation of unsaturated hydrocarbons. Our computations revealed that the mechanism behind the experimentally observed function of amines as selectivity switches in partial hydrogenation of alkynes into alkenes is the difference in changes in the adsorption energetics of alkenes and the amines themselves versus that of alkynes caused by an increase in the coverage of the Pt nanocatalysts by the amine modifiers.

Computational Studies of Solar Water Splitting by Semiconductor Photocatalysts at the Aueous Solution Interface: The Solar Water Splitting Simulation Team (SWaSSiT)

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Funding:	$320,000

PROGRAM SCOPE

The collaborative research team, SWaSSiT, is pursuing computational studies of multiple aspects of solar water splitting (solar fuel generation) using semiconductor photocatalysts in aqueous solution. Heterogeneous solar photocatalysis requires a deep understanding of solid-state properties (band positions, exciton dynamics, charge transport, and trapping) as well as surface structures and properties. This is traditionally the domain of solid-state physics. It also requires great advances in the understanding of charge-driven redox reactions and catalysis at surfaces, traditionally the domain of chemists. This all takes place, in most schemes, at a liquid/solid boundary. While both communities address specific physical properties of this complex interface, the complexity of the photocatalysis problem requires a coordinated approach to under-stand charge generation and transport coupled to the mechanism, energetics, and kinetics of the chemical reactions. The Swassit team, built from an existing core collaboration, includes the essential expertise to engage in computational research, in close consultation with our experimental collaborators, towards: (1) the theoretical understanding of H_2O oxidation at semiconductor-aqueous solution interfaces; (2) the cyber-prediction of bulk and surface crystal structure of new semiconductor materials; and (3) understanding the electron dynamics of charge separation, trapping, and interfacial redox processes.

FY 2012 HIGHLIGHTS

In its first year of operation, SWaSSiT has hired four BNL postdoctoral Research Associates, one stationed at each of the four participating institutions. We hold monthly meetings via Skype and semiannual face-to-face meetings. These are augmented by frequent meetings between the extended BNL and Stony Brook University groups to discuss collaborative work. We have an Advisory Board consisting of one experimental chemist in the field of solar fuels from each of the four participating institutions (Etsuko Fujita, Michael G. White, Gary Brudvig, and Richard Eisenberg) and a computational chemist at large (Annabella Selloni).

Multi-disciplinary computational studies have begun in several areas: water oxidation at a RuO2/aqueous interface; surface reconstructions at a GaZnNO/aqueous interface; water dissociation at a GaZnNO/aqueous interface; band and molecular reduction potential alignment at a semiconductor/aqueous interface; and hole transfer dynamics at a GaN/aqueous interface.

Surface Chemical Dynamics

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Sr. Investigator(s):	Camillone III, Nicholas, Brookhaven National Laboratory
Students:	2 Postdoctoral Fellow(s), 4 Graduate(s), 0 Undergraduate(s)
Funding:	$1,075,000

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 and/or desorption 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 interadsorbate interactions on molecular orbital energies. New 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 clusters from ion beams as well as solution-phase synthesis and deposition of narrow-size-distribution nanometer-scale particles.

FY 2012 HIGHLIGHTS

We have synthesized robust TiO_2-supported Pd NP arrays and found them to be active for adsorption (O_2 and CO) and catalysis (thermal oxidation of CO). Femtosecond photoexcitation of the NPs efficiently drives molecular desorption, and subpicosecond time-resolved dynamics measurements suggest concurrent ultrafast electron-mediated and slower phonon-mediated nanoparticle–adsorbate energy transfer mechanisms.

New state-resolved studies of the photooxidation of simple ketones adsorbed on titania showed how excess energy is channeled into the final state distributions (translation, rotation, vibration) of gas-phase methyl radicals produced during the photoinduced reaction. We also found that the photooxidation of simple alcohols (ethanol and 2-propanol) involves heretofore unobserved secondary photoreactions of ketone or diolate intermediates that also give rise to gas-phase methyl radicals.

We demonstrated that two-photon photoemission (2PPE) can be used as a sensitive probe of charge-transfer at the cluster-support interface via measurements of the coverage-dependent, local work function. For size-selected Mo_xS_y clusters deposited on an ultra-thin alumina film, measured work function shifts suggest that electron tunneling from the underlying NiAl substrate results in cluster "charging" that is dependent on cluster size and opposite to that expected for metal sulfide clusters bonding to alumina.

Condensed Phase and Interfacial Molecular Science

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Sr. Investigator(s):	Ahmed, Musahid, Lawrence Berkeley National Laboratory Chandler, David, Lawrence Berkeley National Laboratory Geissler, Phillip L., Lawrence Berkeley National Laboratory Harris, Charles B., Lawrence Berkeley National Laboratory
Students:	4 Postdoctoral Fellow(s), 6 Graduate(s), 0 Undergraduate(s)
Funding:	$1,364,000

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, 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 2012 HIGHLIGHTS

- Imaging Mass Spectrometry
- Theory of Dynamics in Complex Systems
- Solvation in Heterogeneous Liquid Environments
- Ultrafast Studies of Electron Transport and Molecular Motions at Interfaces
- X-Ray Absorption Spectroscopy of Liquids and Liquid Surfaces, Characterization of Liquid Electrolyte Interfaces by Ultrafast Nonlinear Optical Spectroscopy

Early Career: Free Radical Reactions of Hydrocarbons at Aqueous Interfaces

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Sr. Investigator(s):	
Students:	1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$500,000

PROGRAM SCOPE

Heterogeneous reactions occurring at hydrocarbon/water and electrolyte interfaces govern a wide array of environmentally and technologically important processes, including electrochemistry, aerosol photo-oxidation, cloud chemistry, corrosion, and heterogeneous catalysis. In many of these systems, interfacial hydrocarbon free radicals (e.g., RO_2), formed by species such as hydroxyl radicals (OH) in the presence of O_2, play key chemical roles as initiators or propagators of surface reactions or as reactive intermediates. Simple predictions of interfacial reaction rates and mechanisms extrapolated from homogeneous gas or bulk phase systems have been shown to be highly inaccurate since surface molecular orientation and electronic structure can often alter the activation energy of a reaction occurring at a surface. In order to quantify heterogeneous reaction rates and construct detailed surface reaction mechanisms, two state-of-the-art experimental probes will be developed to study the heterogeneous transformations occurring in and on micron and nanometer sized water-solute droplets exposed to oxygen-containing free radicals, with a particular focus on the reactivity of the droplet-gas phase interface. The atomic and molecular changes in the surface and subsurface (8-20Å) will be quantified using a newly developed droplet train ambient pressure x-ray photoelectron spectrometer. A novel surface sensitive mass spectrometer will be used to make detailed kinetic measurements in order to quantify heterogeneous reaction rates and molecularly specific reaction product distributions. Together these instruments will be used to construct molecularly detailed free radical reaction mechanisms in an effort to develop general theories to better understand how hydrocarbon structure, interfacial solute ions, and their spatial organization at the liquid surface govern molecular weight growth and degradation chemistry of organic molecules at aqueous interfaces.

Kinetics of Charge Transfer in a Heterogeneous Catalyst-Reactant System: The Interplay of Solid State and Molecular Properties

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Sr. Investigator(s):	
Students:	1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$330,000

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 TiO_2, p-type Co_3O_4, and RuO_2). Ferrocene oxidation will be used as a model one electron transfer reaction.

Knowledge-Guided Screening Tools for Identification of Porous Materials for CO_2 Separation

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Students:	0 Postdoctoral Fellow(s), 0 Graduate(s), 2 Undergraduate(s)
Funding:	$50,000

PROGRAM SCOPE

Porous materials have many important applications in the chemical industry. Zeolites, for example, are used for gas separation as well as cracking catalysts in oil refining, alkylation, and isomerization reactions catalysts. Although the number of possible zeolite structures has been estimated to be more than 2.5 million, only about 180 structures have been synthesized to date. The main goal of this proposal is to develop methods that will allow the identification of structures with optimal performance for specific applications, with a focus on predicting new materials for CO2 separation. Although current state-of-the-art molecular simulations allow for accurate prediction of zeolite properties, the characterization of an entire database of hypothetical structures would be out of the question even with today’s supercomputers. This proposal presents an approach that will allow the screening of large databases of structures. Only structures that are predicted to exhibit properties of interest are subjected to a follow-on characterization using the more accurate but also more expensive molecular simulation methodology. We propose to select structures to undergo characterization using knowledge-based techniques. First, those structural aspects that govern a selected property are identified. Then the structures in the database are clustered to identify similar structures, and all structures similar to those that have a poor performance are eliminated. A refined set of structural descriptors and similarity measures is then computed based on the new information gleaned from the molecular simulations. The process is repeated until the optimal structures with the desired properties have been identified.

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

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Funding: $116,000

PROGRAM SCOPE

We will create a Nanoporous Materials Genome Center (NMG). The NMG will be organized around a novel class of materials, namely metal-organic frameworks, MOFs, that have many interesting properties and offer high-payoff opportunities from a computational design point of view.

The NMGC will develop and employ state-of-the-art computational tools to characterize and predict the performance of millions of as-yet-unsynthesized materials, and it will provide a repository of experimental structures and associated properties. The NMG, continuously validated against experiment, will serve to integrate materials discovery, materials design, materials characterization, and functional performance.

The Center will bring together 11 theoretical chemists and chemical engineers and 4 experimentalists, whose combined expertise will cover all the areas needed for a unique collaborative effort.

The following chemical challenges will be addressed: (1) separation of N_2/O_2 in open-site MOFs, (2) separation of N_2/CO_2 in amine containing MOFs, (3) stimulus-responsive materials, (4) alkane activation in MOFs, and (5) MOFs containing metal ions in unprecedented coordination environments.

In order to study these problems, we will organize the computational research into two thrusts. Thrust I will consist of developing and employing quantum chemical methods able to treat strong electron correlation effects and excited states in MOFs and able accurately to treat weak, non-bonded interactions. These methods will range from state-of-the-art multireference wave function theory models to density functional theory based on modern functionals. Photochemical dynamics will be included as part of studying the interaction of these materials with radiation.

Thrust II will ensure that the predictions made are robust and reliable. It will consist of the development and employment of tools for the generation of a large number of hypothetical structures for MOFs and for the screening of the database for optimal performance. We will use the high-level quantum calculations developed in Thrust I to derive accurate force fields to predict the properties of the adsorbed molecules (adsorption isotherms, diffusion coefficients, etc) and properties of the materials (e.g., flexibilities of the structures).

The final goal of the NMG is to develop a software solution able to screen millions of different materials for a given application. For most applications, it would be far too expensive to compute all properties for a given performance. As part of Thrust II, we aim to develop heuristic algorithms for sophisticated data mining and screening.

At the end of the project, the NMG will be a publically accessible repository of measured and predicted properties joined to a set of user-friendly computational tools for adding to the database in an ongoing, self-learning fashion.

Simulating the Generation, Evolution, and Fate of Electronic Excitations in Molecular and Nanoscale Materials with First Principles Methods

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Students:	3 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$780,000

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.

Next Generation First Principles Molecular Dynamics

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

PROGRAM SCOPE

As the processing power available for scientific computing grows, first principles Born-Oppenheimer molecular dynamics simulations are becoming increasingly important for the study of a wide range of problems related to our future energy needs in materials science, chemistry, and biology. Nevertheless, the computational cost of Born-Oppenheimer molecular dynamics still remains prohibitively large for many important problems. The overreaching goal of this proposal is to go beyond conventional Born-Oppenheimer molecular dynamics and create a framework for a new generation of quantum mechanical molecular dynamics 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 2012 HIGHLIGHTS

For the very first time, we have managed to combine microcanonical (energy conserving) Born-Oppenheimer molecular dynamics simulations with low pre-factor linear scaling algorithms [J. Chem. Phys. 137, 134105 (2012)]. This is a crucial breakthrough that shows that accurate and reliable quantum mechanical molecular dynamics simulations are possible also for very large complex systems. Previous attempts have shown systematic drifts in the energy that are 3 to 5 orders of magnitude larger than any of our current estimates. An efficient full parallelization (beyond the scope of the current proposal) may allow simulations of a million atoms and time steps even on a fairly modest computational platform.

We have also demonstrated how to circumvent a major computational bottleneck in Born-Oppenheimer molecular dynamics simulations arising from the required self-consistent-charge optimization [http://arxiv.org/abs/1203.6836v2, accepted in Phys. Rev. B]. The new approach is based on extended Lagrangian Born-Oppenheimer molecular dynamics in the limit of vanishing self-consistent field optimization. The molecular trajectories are virtually indistinguishable from “exact” Born-Oppenheimer dynamics even when low pre-factor linear scaling sparse matrix algebra is used. Our findings show that the computational gap between classical and quantum mechanical molecular dynamics simulations can be significantly reduced.

Charge Transfer and Charge Transport in Photoactivated Systems: Developing Advanced Methods for Excited State Chemistry in the NWChem Software Suite

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Funding:	$200,000

PROGRAM SCOPE

A suite of new theoretical methods will be 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).

Specifically in this project, the goal is to implement new advanced methods and algorithms centered for (1) multistate complete-active-space second-order perturbation theory including relativistic effects,

(2) the treatment of electronically nonadiabatic and ultrafast dynamics in both the gas-phase and solution, (3) state-specific non-equilibrium and equilibrium continuum solvation effects for the computation of excited-state wave functions, (4) electrostatically embedded multiconfiguration molecular mechanics and molecular mechanics (EE-MCMM/MM) schemes, (5) approaches for the treatment of explicit local solvation environments but further embedded to include longer-range solvent effects, and (6) Monte Carlo strategies for efficient conformational sampling of chromophores.

Chemical Kinetics and Dynamics at Interfaces

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Students:	5 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$3,372,000

PROGRAM SCOPE

The Condensed Phase and Interfacial Molecular Science (CPIMS) 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 2012 HIGHLIGHTS

Research highlights in FY 2012 include (1) the development of an inert gas permeation experimental technique and scaling model to determine the diffusivities of supercooled liquids near their glass transition temperatures; (2) the discovery of a new photon induced reaction between chemisorbed O_2 and physisorbed O_2 on the surface of the important photocatalyst, rutile TiO_2; (3) the combination of x-ray absorption fine structure (XAFS) experimental techniques and molecular dynamics simulations to improve our understanding of the water-ion and ion-ion structure relevant to a broad range of chemical, geochemical, biochemical, and atmospheric processes; (4) the first gas-phase spectroscopic characterization of Zeise's anions and measurement of ion specific interactions between alkali cations and dicarboxylate dianions, important in understanding the transport in ion channels in cells; and (5) the combination of scanning and photoemission electron microscopy (SEM & PEEM) images to determine structure-specific electric field enhancements, due to localized surface plasmons, of correlated silver nanoparticles.

Molecular Theory and Modeling

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Sr. Investigator(s):	Dang, Liem, Pacific Northwest National Laboratory Dupuis, MIchel, Pacific Northwest National Laboratory Garrett, Bruce, Pacific Northwest National Laboratory Kathmann, Shawn, Pacific Northwest National Laboratory Mundy, Christopher, Pacific Northwest National Laboratory Valiev, Marat, Pacific Northwest National Laboratory Xantheas, Sotiris, Pacific Northwest National Laboratory Ginovska-Pangovska, Bojana, Pacific Northwest National Laboratory
Students:	2 Postdoctoral Fellow(s), 3 Graduate(s), 0 Undergraduate(s)
Funding:	$2,375,000

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 2012 HIGHLIGHTS

We are developing techniques to understand the "specific ion effect" and are developing a detailed molecular understanding of the driving forces of ions to hydrophobic interfaces. This has far-reaching implications in disciplines ranging from biology to understanding the stability of colloidal suspensions. Furthermore, we are applying these techniques to make direct comparisons to detailed experimental measurements using vibrational spectroscopy, x-ray absorption fine structure, and x-ray and neutron diffraction. We are developing meso-scale principles to connect details of molecular interaction to processes of self-assembly. We are extending our techniques to better understand the structure of concentrated electrolytes and the characterization of electric fields in matter. We continue to use high-level electronic structure calculations on realistic systems to establish accurate benchmarks. This has impacted the understanding of gas accommodation in hydrate lattices.

Gas-Phase Chemical Physics

Institutions Receiving Grants

Dynamics of Large Amplitude Motion in Energized Molecules

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Sr. Investigator(s):	
Students:	1 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$122,000

PROGRAM SCOPE

In the 21st century, transportation fuel stocks will be more complex and more variable. The combustion conditions in practical engines will include temperatures, pressures, and compositions far from accessible experimental measurements. Therefore, predictive combustion codes must rely on theories of reaction rates that can reliably extrapolate well beyond the domain of measured data. In order to contribute to that goal, the proposed research evaluates one of the underlying assumptions of reaction rate theories. Chemical reactions, by their nature, involve large-amplitude motion of the nuclei, and theories of reaction rates invoke a separation of variables between the large-amplitude (i.e., reactive) motion and the other small-amplitude vibrations. This work evaluates the limits of validity of approximate separations of the nuclear degrees of freedom and explores the nature of the couplings between degrees of freedom.

This project probes the dynamics that result from the coupling between nuclear degrees of freedom in molecular systems with two (or more) large amplitude degrees of freedom. To access the precision and detail available from high-resolution spectroscopy, large-amplitude degrees of freedom in bound molecular systems are used as model reaction coordinates. Methylamine has six equivalent minima connected by torsional and inversion tunneling pathways. In infrared spectra, excitation of CH or NH stretch vibrations changes the pattern of the torsion-inversion structure, and these changes serve as a probe of the coupling between the degrees of freedom. Model calculations are used to interpret the molecular dynamics revealed in the spectra and to look for systematic trends across related molecular systems. Other large-amplitude systems to be investigated include acetylene, ethyl radial, protonated methanol, nitomethane, and 2-methylmalonaldehyde. This project aims to provide an understanding of when approximate separations of degrees of freedom are valid and when multi-dimensional treatments are essential.

FY 2012 HIGHLIGHTS

High-resolution slit-jet spectra in the asymmetric CH stretch region of methylamine were analyzed and interpreted in terms of the interacting rotational, torsional, inversion, and CH stretch degrees of freedom. Both simple model calculations of the resulting torsion-inversion level structures and more sophisticated calculations of the quantum dynamics on *ab inito* potential energy hypersurfaces have been undertaken. These calculations, although initially focused on methylamine, are being extended to a range of large-amplitude systems. In collaboration with Michel Herman of the Free University of Brussels, the high-resolution rotation-vibration transitions of acetylene up to 13,000 cm-1 have been fitted to a polyad Hamiltonian. This detailed spectroscopic Hamiltonian allows the intramolecular dynamics that would follow preparation of different initial vibrations. Hierarchies of detailed dynamical pathways are revealed. Infrared spectra of nitromethane from the Pacific Northwest National Laboratory and from the Canadian Light Source are being analyzed in terms of the 6-fold rotor dynamics.

Probing Chemical Dynamics by Structurally Sensitive Photoionization

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Sr. Investigator(s):	
Students:	0 Postdoctoral Fellow(s), 3 Graduate(s), 1 Undergraduate(s)
Funding:	$145,000

PROGRAM SCOPE

The research program explores the chemical reaction dynamics of molecular model systems that are relevant to combustion reactions. Driven by the importance of understanding the chemical processes unfolding during combustion, our research seeks to investigate the motions of, and energy flow within, molecules while they react.

To enable the investigations, we have developed a new spectroscopic technique that takes advantage of the fact that photoionization through Rydberg states, coupled with the measurement of the electron binding energies by photoelectron spectroscopy, provide very clear spectral signatures of molecular structures. Among the many unique attributes of this technique are the spectra are sensitive to the global molecular structure even in large molecules, while being extraordinarily insensitive to vibrational motions and thus thermal excitation.

Current investigations focus on electronic curve crossing dynamics in cyclohexadiene, the ultrafast dynamics of flexible model systems. Among the latter systems, we explore molecular compounds with internal degrees of freedom that need to be activated as part of intramolecular chemical reactions, and on molecular clusters.

FY 2012 HIGHLIGHTS

In measurements on the photodissociation dynamics of amyl nitrite, we explored the photoionization and photofragmentation dynamics of a nitrite. It was well known that upon electronic excitation, the NO entity dissociates from the aliphatic hydrocarbon on a repulsive surface. What was new and exciting is that, when excited to the S_2 surface, there is an even faster internal conversion that brings the molecule to the S_1 surface, on which it then dissociates. If confirmed in other molecules, this observation could lead us to re-evaluate our understanding of the photodissociation dynamics on highly excited surfaces.

Separately, we have explored the interconversion of quadricyclane to norbornadiene, a system of highly energetic hydrocarbons. We measured the energy flow across Rydberg surfaces and mapped the flow of the wave packet across the potential energy landscape.

Modeling Reactions in High-Pressure Turbulence in the Cold Ignition Regime

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Students:	1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$125,000

PROGRAM SCOPE

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 typical of the auto-ignition regime, with particular emphasis on the manifestation of this coupling on the effective kinetic rate.

FY 2012 HIGHLIGHTS

We have created a database of eight direct numerical simulations of a temporal mixing layer created between two counter-flow streams: air mixed with water and carbon dioxide in the upper stream at 1000 K temperature and n-heptane with water and carbon dioxide in the lower stream at 600 K temperature. The initial Reynolds number, the free-stream pressure, and the amounts of water and carbon dioxide were varied among simulations. We (1) developed a methodology for defining and computing effective Schmidt and Prandtl numbers and (2) found that species spinodal decomposition may occur and determined the necessary and sufficient conditions for it to occur.

Towards Predictive Simulations of Soot Formation: From Surrogate to Turbulence

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Sr. Investigator(s):	
Students:	1 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding:	$160,000

PROGRAM SCOPE

The aim of this project is to fill the gap in the present understanding and modeling of soot formation both in laminar and turbulent flames. The project focuses on the combustion of surrogate fuels comprised of several chemical species in contrast to current single-species models. Our current state-of-the-art chemical model will be extended with additional components often found in surrogates. The inner structure of soot particles will be investigated as a means to gain insight into soot inception, growth, and oxidation via the development of a nested hierarchy approach combining quantum chemistry, molecular dynamics, and Monte Carlo simulations. The newly improved chemical and soot models will be incorporated in direct numerical simulations of turbulent sooting flames and validated in turbulent jet diffusion flames. The outcome is expected to be a major leap in the development of predictive models for the combustion of transportation fuels, the formation/oxidation of soot, and large eddy simulations. The impact of the proposed research goes far beyond soot formation. It is relevant to the formation of all other nanoparticles (SiO_2, TiO_2, and AlO3) as well as other slowly evolving processes in turbulent flows (CO, NO_x).

Determination of Accurate Energetic Database for Combustion Chemistry by High-Resolution Photoionization and Photoelectron Methods

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Students:	1 Postdoctoral Fellow(s), 3 Graduate(s), 0 Undergraduate(s)
Funding:	$150,000

PROGRAM SCOPE

The main goal of this research program is to obtain accurate thermochemical and spectroscopic data, such as ionization energies, 0 K bond dissociation energies, 0 K heats of formation, and spectroscopic constants for radicals and molecules and their ions of relevance to combustion chemistry. Two unique vacuum ultraviolet (VUV) laser photoion-photoelectron apparatuses have been developed, which will be employed in the proposed studies. In additional to performing VUV laser photoionization efficiency and pulsed filed ionization-photoelectron (PFI-PE) measurements, we plan to employ two-color infrared (IR)-VUV laser photoion-photoelectron schemes for high-resolution state-selected and resolved PIE and PFI-PE measurements of polyatomic species. The single mode IR-VUV laser photoion (IR-VUV-PI) scheme has also been demonstrated to be a very sensitive method for high-resolution IR spectroscopic measurements of polyatomic species. A high-resolution VUV laser velocity-map imaging–photoelectron (VMI-PE) and VMI-threshold photoelectron technique has been demonstrated to achieve an energy resolution of 2 cm^{-1} (FWHM). The high sensitivity of the PFI-PE method makes it promising for high-resolution photoelectron measurements of radicals. In the next funding cycle, we shall focus on photoion-photoelectron measurements of selected combustion radicals, including sulfur monoxide (SO), ethynyl (C_2H), propargyl (C_3H_3), allyl (C_3H_5), 1-buten-3-yn-1-yl [HC≡C-CH=CH], *o*-benzyne (*o*-C_6H_4), phenyl (C_6H_5), and phenoxyl (C_6H_5O) radicals, along with halogenated hydrocarbon methyl (CH_2X) and CHXY and methylene (CHX) (X, Y=F, Cl, Br, and I) radicals. Using a newly developed VUV laser VMI-PI apparatus, we are also interested in examining the dynamics of laser photodissociation reactions of relevance to the production of combustion radicals. The high-resolution VUV laser PFI-PI and VUV Rydberg tagging time-of-flight techniques developed in our laboratory will be employed in the photodissociation studies.

FY 2012 HIGHLIGHTS

By employing the VUV laser VMI-PE method, we have obtained a vibrationally resolved photoelectron spectrum of gaseous propargyl radical [$C_3H_3(X^2B_1)$] in the energy range of 0-4,600 cm^{-1} above its ionization energy. The cold C_3H_3 radicals were produced from a supersonically cooled radical beam source based on 193 nm ArF photodissciation (PD) of C_3H_3Cl. The VUV-VMI-PE spectrum of C_3H_3 thus obtained reveals a Franck-Condon factor (FCF) pattern with a highly dominant origin band along with weak vibrational progressions associated with excitations of the C–C $\nu_5^+(a_1)$ and C≡C $\nu_3^+(a_1)$ symmetric stretching modes and the CCH $\nu_7^+(b_1)$ out-of-plane bending mode of $C_3H_3^+(X^1A_1)$. The $\nu_5^+(a_1)$ vibrational frequency of 1120 cm^{-1} determined in the present study is lower than the value deduced from the recent Ar-tagged infrared photodissociation study by 102 cm^{-1}, confirming the highly accurate vibrational frequency predictions obtained by the most recent state-of-the-art *ab initio* quantum calculations. The observation of the FCF disallowed $\nu_7^+(b_1)$ mode is indicative of vibronic interactions.

Dynamics and Energetics of Elementary Combustion Reactions and Transient Species

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Funding:	$150,000

PROGRAM SCOPE

This research program pursues unique studies of transient neutral species and collision complexes relevant to combustion phenomena. The experimental approach involves photodetachment of precursor molecular and cluster anions, allowing direct measurements of the stability and dissociation dynamics of energy-selected reactive intermediates. This technique combines photoelectron spectroscopy with photofragment translational spectroscopy to yield the combined technique of photoelectron-photofragment coincidence spectroscopy. In the second year of this grant, we have continued to exploit a new cryogenic electrostatic ion beam trap (CEIBT) to study the photoelectron spectra and examine the dissociative photodetachment processes of cooled anion precursors of species important to combustion processes. Using this new apparatus, we have carried out a number of important experiments on reactive intermediates important to combustion processes, including HOCO, HCO_2, and larger oxygenated radicals. The primary effort currently underway on the apparatus involves preparation of vibrationally excited anions prior to injection in the trap as discussed below. During the final year of the present grant, the primary focus will be on pursuing the experiments on vibrational excitation of the precursor anions.

FY 2012 HIGHLIGHTS

A number of important milestones were achieved in FY 2012. A report documenting the new CEIBT apparatus was published in the *Review of Scientific Instruments*, and important advances in understanding the energetics and structure of HOCO and $HOCO^-$ were reported in a communication in the *Journal of the American Chemical Society*. New results on the state-resolved predissociation dynamics of the formyloxyl radical (HCO_2) have been obtained, providing insight into the dynamics of another important region on the HOCO potential energy surface. The extension of these types of measurements to larger oxygenated species relevant to the oxidation of biofuels has been achieved in a study of the tert-butoxy radical (C_4H_9O) and radicals produced by photodetachment of a carbanion isomer. Finally, we have assembled a facility for vibrationally exciting the precursor anions prior to injection into the CEIBT and are currently searching for a signal from the vibrationally excited species, with a focus on the $OH^-(H_2O)$, $F^-(H_2O)$, $Cl^-(H_2O)$, and $I^-(H_2O)$ series of clusters. Successful completion of this effort will open the door to a deeper understanding of the role of vibrational excitation in the reaction dynamics of transient combustion intermediates.

Dynamics of Product Branching in Elementary Combustion Reactions: OH + Alkenes and Nitrogen Chemistry

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Funding:	$163,000

PROGRAM SCOPE

The elementary reactions that determine the performance of a combustion system range from direct H-atom abstraction reactions to complex reactions involving competing addition and abstraction mechanisms and branching to multiple product channels with a strong temperature and pressure dependence. While the total rate constant for many elementary reactions is well-characterized, our experiments are designed to elucidate the dynamics of the branching to product channels resulting from additional mechanisms in bimolecular reactions. With crossed laser-molecular beam scattering experiments and velocity map imaging measurements, we generate a particular isomeric form of an unstable radical intermediate along the bimolecular reaction coordinate and investigate the branching between the ensuing product channels as a function of the radical intermediate's ro-vibrational energy under collision-less conditions. The results develop insight on product channel branching in such reactions and provide a benchmark for emerging electronic structure calculations on polyatomic reactions that proceed through unstable radical intermediates. They also offer experimental data to benchmark elements of the master-equation modeling of the temperature-dependent product branching in elementary combustion reactions.

FY 2012 HIGHLIGHTS

The most exciting work this year built on our results from the prior grant period that resolved the branching to three competing channels of the OH + ethene reaction from the CH_2CH_2OH radical intermediate: CH_3+formaldehyde, H + ethenol, and vinyl + H_2O. Our new experiments, published this past year, were designed to test the influence of tunneling by measuring the product branching when the radical intermediate is partially deuterated to CD_2CD_2OH. That work revealed that angular momentum plays a key role in the product branching. We have edited our collaborator's (J. Bowman) classical trajectory code to allow us to make a prediction for the product branching using initial conditions that accurately represent the nascent radicals that we produce photolytically. We have also undertaken a study of the photodissociation dynamics of 2-bromo-ethylnitrite ($BrCH_2CH_2ONO$) at 351 nm. This project was initiated to assist our collaborator (T. A. Miller), whose DOE-supported project uses XCH_2CH_2ONO (X = Br, Cl, OH) to study the radical intermediates important in atmospheric chemistry involving hydrocarbon radicals, OH, and NO_2. Our experiments characterize the primary photodissociation channels of the radical precursor and identify the product branching from the radical intermediates of interest. The data serves to benchmark electronic structure calculations of barriers in radical reactions.

Spectroscopy, Kinetics, and Dynamics of Combustion Radicals

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Funding: $50,000

PROGRAM SCOPE

The goal of this research program is the combined experimental and theoretical study of chemical transient species relevant to fundamental combustion processes, based on (1) intense discharge/photolysis sources of jet-cooled radicals, (2) controlled formation and trapping of combustion intermediates by supersonic cooling, and (3) high sensitivity detection with direct IR laser absorption and/or REMPI/velocity map imaging (VMI) methods. A key advantage of this approach is that high concentrations of radicals are formed under moderate pressure combustion conditions, allowed to react with reagents to form new radicals and/or products, with the resulting species rapidly concentrated into the lowest quantum states ($T \approx 10$-20K) and detected immediately downstream in the slit supersonic expansion. The generality of IR laser absorption methods makes this a particularly powerful combination, offering high resolution spectral access to critical radical intermediates and nascent combustion products, as well as providing both high sensitivity and absolute radical densities with which to help elucidate complex branching pathways.

FY 2012 HIGHLIGHTS

In the past year, we have successfully detected and analyzed high resolution spectra of several key combustion species, including hydroxymethyl (CH_2OH) and phenyl (C_6H_5) radicals. With regard to hydroxymethyl radical, high resolution, fully rotationally resolved direct absorption spectra have been obtained in the infrared CH stretching region. As a result of low rotational temperatures and sub-Doppler linewidths obtained in the slit supersonic expansion, the $K_a = 0 \leftarrow 0$ band of the symmetric CH stretch for CH_2OH has been unambiguously identified and analyzed. The identified 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 improve upon spectral efforts via previous double resonance ionization detected IR methods by Feng et al, which obtained partially rotationally resolved spectra in both the CH and OH stretching regions.

The phenyl radical has also been studied with high-resolution infrared spectroscopy enabling the identification of the $v = 1 \leftarrow 0$ excitation of the C-H symmetric out-of-phase vibration, ν_{19}. This assignment is unambiguously confirmed via comparison with ground state combination differences calculated from microwave data, with energies matching to within 6 MHz (2.0×10^{-4} cm^{-1}). Despite having 11 atoms and 27 vibrational modes, phenyl radical has an IR spectrum that is surprisingly simple; it lacks broadening due to intramolecular vibrational relaxation (IVR) and exhibits no measurable perturbations due to nearby states. In addition, the planarity and symmetry of phenyl radical are confirmed through nuclear spin statistical weighting and inertial defect. The success of this analysis offers extremely hopeful prospects for high resolution infrared spectroscopy of increasingly large (>10 atom) aromatic hydrocarbon radicals in complex combustion environments.

Atomic Scale Imaging of the Electronic Structure and Chemistry of Graphene and Graphite

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Funding:	$100,000

PROGRAM SCOPE

The goals of this project are to reveal the mechanisms and reaction processes that solid carbon materials undergo when combining with gases such as oxygen, water vapor, ammonia, and hydrocarbons. This research is focused on fundamental chemical events taking place on single carbon sheets of graphene, a two-dimensional, polycyclic carbon material that possesses remarkable chemical and electronic properties. Ultimately, this work is related to the role of these materials in mediating the formation of polycyclic aromatic hydrocarbons (PAH's), their reactions at interfaces, and the growth of soot particles. Our intent is to contribute to a fundamental understanding of carbon chemistry and the mechanisms that control the formation of PAH's, which eventually lead to the growth of undesirable particulates.

Our work treats, specifically, the surface chemistry aspects of carbon reactions by using proximal probe (atomic scale imaging) techniques to study model systems of graphene that have many features in common with soot forming reactions of importance in combustion flames. Scanning tunneling microscopy is the main probe technique that we use to study the interfacial structure and chemistry of graphene, mainly because of its ability to elucidate surface structure and dynamics with atomic resolution. Scanning tunneling spectroscopy, which measures the local density of quantum states over a single atom, provides information about the electronic structure of graphene and is particularly sensitive to the sign and magnitude of the charge transfer between graphene and any surface adsorbed species.

FY 2012 HIGHLIGHTS

We have shown that graphene can be grown more efficiently on a Cu (100) surface than on a Cu (111) surface and that graphene will react with NH_3 on such a surface to incorporate N atoms into the graphene lattice. Visualization of the N atoms on the surface shows that they are slightly elevated (~ 0.8 Å) above the graphene plane. On average, each N atom donates ~ 0.4 electrons to the graphene lattice and the concentration of nitrogen is ~ 3N/1000C. This concentration can be controlled by varying the partial pressure of NH_3 during CVD growth. In the next period, we envision pursuing efforts designed to unravel aspects of the mechanisms for chemistry on graphene surfaces, by investigating the oxidation pathway for single "pristine" graphene sheets grown in an ultra-high vacuum chamber on a copper surface using chemical vapor deposition techniques and by studying the mechanism for assembly of graphene flakes from smaller Polycyclic Aromatic Hydrocarbons such as hexabenzocoronene on cobalt, copper (111), and copper (100) surfaces.

Computational Flame Diagnostics for Direct Numerical Simulations with Detailed Chemistry of Transportation Fuels

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Funding:	$300,000

PROGRAM SCOPE

The goal of the proposed research is to create computational flame diagnostics (CFLD) that are rigorous numerical algorithms for systematic detection of critical flame features and the underlying physicochemical processes controlling them. Critical flame features such as ignition, extinction, flame fronts, and stabilization mechanisms will be extracted using CFLD from DNS datasets to understand the complex flame behaviors related to fuel efficiency and emissions. The goal will be accomplished through (1) creating and tuning non-stiff reduced mechanisms for transportation fuels, including n-hepatane, n-dodecane and biodiesel surrogates, that are amenable for three-dimensional DNS; (2) performing DNS for turbulent lifted flames, laminar sooting flames, and auto-igniting flames at homogeneous charge compression ignition (HCCI) conditions; (3) developing CFLD based on chemical explosive mode analysis (CEMA) recently developed by the PI to systematically extract critical flame features from the massive DNS datasets; (4) utilizing the DNS results to improve turbulent mixing and combustion modeling for large eddy simulations; and (5) developing systematic methods based on chemical kinetics for DNS data reduction, such that the datasets can be efficiently reduced and reconstructed without significant loss of chemical information. The reduced DNS datasets can then be readily shared with the community.

FY 2012 HIGHLIGHTS

The program started on September 1, 2012. Reduced mechanisms for transportation fuels are being prepared for the proposed tasks (1-3).

Bimolecular Dynamics of Combustion Reactions

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Funding:	$150,000

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, a molecular beam containing highly reactive free radicals is crossed with a second molecular beam. The angular and velocity distributions of the neutral products from single reactive collisions are measured using “universal” mass spectrometry with single photon pulsed vacuum ultraviolet (VUV) photoionization, or for reactions leading to H, D, or O atom products, by Rydberg tagging time-of-flight methods.

FY 2012 HIGHLIGHTS

We have continued our studies of reactions of phenyl radicals (C_6H_5) with molecular oxygen (O_2), as well as with propene (C_3H_6) and butene (C_4H_8), using 10.5 eV photoionization detection of products. Experimental conditions have also been optimized for studies of the reaction $H + O_2 \rightarrow OH + O$, using the O atom Rydberg tagging method. We have extended the energy range of our tabletop VUV light sources to 13.5 eV by combining noncollinear phasematching with pulsed laser vaporization of metals. We expect this new VUV source will be extremely valuable for our upcoming studies of the competing product channels from elementary bimolecular reactions of alkyl radicals with molecular oxygen.

Investigation of Non-Premixed Turbulent Combustion

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Funding:	$146,000

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, and the maximum number of chemical species that can be handled is about 40, thus limiting the approach to simple fuels with relatively small chemical mechanisms. The overall objective of this project is to develop and demonstrate an adaptive chemistry approach for use in particle PDF and LES/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 the time required for a computation with a given detailed mechanism and enabling affordable computations with significantly larger detailed mechanisms. Rather than performing chemical reduction at runtime to determine the optimal set of equations to use for a given particle, a time consuming task that limits the benefits of the adaptive approach, an *a priori* analysis of the composition space region likely accessed during the turbulent combustion flow simulation, is performed using simple Partially Stirred Reactor (PaSR) computations. This analysis aims at partitioning the composition space into a pre-defined number of regions and identifying for each of them a reduced kinetic model much smaller than the detailed mechanism using conventional reduction techniques such as graph search algorithms and dimension-reduction methodologies. Simple classification criteria are then used at runtime to associate particles with a suitable reduced model from this pre-defined set. The long-term goal is to couple the adaptive strategy with In Situ Adaptive Tabulation and demonstrate the method's potential to handle complex fuels chemical kinetics.

FY 2012 HIGHLIGHTS

In the first three months of this project, we successfully developed and implemented a base algorithm containing all the major components of the method. Satisfactory results have been obtained in PaSR for non-premixed methane and propane combustion. In the next period, we are planning to improve and thoroughly characterize the accuracy of the approach and perform preliminary tests in three-dimensional turbulent configurations.

Theoretical Studies of Combustion Dynamics

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Funding:	$130,000

PROGRAM SCOPE

The goals of this project are to develop and apply theoretical and computational methods to study the dynamics of chemical reactions, energy transfer, and recombination of systems relevant to gas-phase combustion chemistry. Radicals play a central role in hydrocarbon combustion, as they are the highly reactive intermediates in the path from fuel plus oxygen to the final products, plus the energy released. Association reactions of radicals, in which stable complexes form via stabilization with a third body, are thus important processes to consider. For the molecular systems relevant to combustion, these are very challenging processes to study with rigorous dynamical methods. In this project, studies will use state-of-the-art, full-dimensional global *ab initio*-based potential energy surfaces to study recombination in $H+C_2H_2$, OH+CO, and NO_2+OH with third bodies. Dynamics calculations (presently quasiclassical molecular dynamics) will be carried using these surfaces to obtain properties such as the energy transfer, isomerization, branching ratios to possibly new fragments, etc. Other quantities of importance to the study of recombination are the partition functions and the infrared spectra. These will also be calculated for the above systems as well as CH_3OH and C_2H_4 using newly developed software. The results of these calculations will be compared to detailed experiments that have recently been done or are being planned, and together, theory and experiment will advance both the understanding and predictive power of combustion reaction dynamics.

FY 2012 HIGHLIGHTS

New complex potential energy surfaces and dynamics calculations were reported for the $O(^3P)+C_2H_4$ reaction including the coupling to the singlet potential. These state-of-the-art calculations were done in collaboration with an experimental group that determined the branching into a variety of products using molecular beam experiments. The agreement with experiment was excellent and helped to elucidate the important dynamical details of this important prototypical combustion reaction.

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:	$110,000

PROGRAM SCOPE

In this project, we investigate complex chemical mechanisms of PAH formation and growth via theoretical studies of their critical elementary reactions. Our primary objectives include the following: (1) to unravel reaction mechanisms through detailed, accurate, and reliable calculations of pertinent potential energy surfaces (PESs); (2) 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; and (3) 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, G4, 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. The underlying theme of the current project period concerns the reactions of phenyl and cyclopentadienyl radical, which are able to produce the smallest PAH and CP-PAH molecules, naphthalene and indene, respectively. In addition, we investigate a variety of oxidation reactions competing with the PAH growth.

FY 2012 HIGHLIGHTS

We have employed chemically accurate ab initio calculations to investigate potential energy surfaces for the reactions of phenyl radical with C3 and C4 unsaturated hydrocarbons and utilized the computed surfaces for kinetics calculations (RRKM and RRKM/ME) to predict reaction rate constants and product branching ratios under various conditions, including single-collision conditions (at the zero-pressure limit) and thermal conditions (at finite pressures and temperatures relevant to combustion flames). The results demonstrated that the reactions of C_6H_5 with C_3H_4, C_4H_4 (vinylacetylene), and C_4H_6 (1,3-butadiene) can lead to the formation of prototype polycyclic aromatic hydrocarbon molecules indene, naphthalene, and 1,4-dihydronaphthalene, respectively. The reactions of 1- and 2-naphthyl radicals with molecular oxygen have been also investigated, and the results showed that at typical combustion conditions, the reactions can produce 1- and 2-naphthoxy radical + O, C_9H_7 (indenyl) + CO_2, 1,2-$C_{10}H_6O_2$ (1,2-naphthoquinone) + H, and 1-/2-C_9H_7O (1-/2-benzopyranyl) + CO.

Theoretical Studies of Elementary Hydrocarbon Species and Their Reactions

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Funding: $202,000

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^{-1}) 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 2012 HIGHLIGHTS

Representative research topics recently pursued are as follows:

(1) The ubiquitous reactions of alkyl radicals with O_2 rapidly become more complex as the radical grows in size. Isomerizations to hydroperoxyalkyl radicals (QOOH) are in competition with concerted elimination of HO_2. In a herculean investigation, all chemically relevant minima and transition states of the *n*-propyl and *i*-propyl + O_2 systems were mapped out using CCSD(T)/cc-pVTZ theory, and focal point analyses targeting the complete basis set limit of CCSDT(Q) were executed to obtain definitive energetics.

(2) Environmental, toxicological, and fundamental scientific concerns continue to drive research on soot formation, which centers around the growth of polycyclic aromatic hydrocarbons (PAHs). The best candidate PAH precursors are resonance-stabilized free radicals, whose enhanced stability and resistance to attack by O_2 allow the buildup of significant concentrations under typical flame conditions. The allyl + propargyl and benzyl + propargyl reaction systems have been systematically studied as alternatives to the propargyl + progargyl route for production of aromatics in aliphatic flames.

(3) A rigorous hierarchy of reaction classes (isogyric, isodesmic, hypohomodesmotic, homodesmotic, hyperhomodesmotic) was constructed, with each type successively conserving larger groups of atoms. This hierarchy was demonstrated to be highly accurate for computing enthalpies of formation of larger hydrocarbons by means of generalized bond separation reactions.

(4) The hydroxycarbenes are archetypical donor-substituted carbenes that are key intermediates in the high-energy chemistry of carbonyl compounds. A synergy between our theoretical research and a German experimental group led to the first successful preparations of hydroxycarbenes by means of high-vacuum flash pyrolysis followed by immediate matrix isolation. This achievement spawned the surprising discovery that hydroxycarbenes can spontaneously disappear within a few hours by pure

quantum mechanical tunneling under large barriers of about 30 kcal/mol, even at very low temperatures. Moreover, methylhydroxycarbene demonstrates the concept of tunneling control, in which the observed product is neither the one requiring the lowest activation barrier nor the one with the lowest free energy, but rather the one most readily reached by quantum mechanical tunneling.

Vibrational Spectroscopy of Transient Combustion Intermediates Trapped in Helium Nanodroplets

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Funding:	$150,000

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 2012 HIGHLIGHTS

We have constructed a pyrolysis source for the production of hydrocarbon radicals for doping helium nanodroplets. We have measured high-resolution vibrational spectra of methyl, vinyl, ethyl, and propargyl radicals, and have shown that it is feasible to measure spectra of the products of the association reactions between these small hydrocarbon radicals and dioxygen. We are finalizing a source of Cl atoms for hydrogen abstraction reactions of closed-shell hydrocarbon molecules within helium nanodroplets, which will allow us to synthesize, in-situ, the elusive QOOH, hydroperoxyalkyl radicals.

Probing the Reaction Dynamics of Hydrogen-Deficient Hydrocarbon Molecules and Radical Intermediates via Crossed Molecular Beams

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Funding:	$141,000

PROGRAM SCOPE

The objectives of this project are to understand the formation mechanisms of prototype *bicyclic* polycyclic aromatic hydrocarbons (PAHs) and their successive growth to *tricyclic* PAHs in combustion processes of hydrocarbon-based fuel. The formation and growth mechanisms of PAHs present a major 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 under single collisions utilizing the crossed molecular beam approach. Our studies focus on four key systems:

(1) We untangle the collision energy-dependent reaction dynamics of key RSFRs [propargyl (H_2CCCH; C_3H_3), cyclopentadienyl (c-C_5H_5), and benzyl ($C_6H_5CH_2$; 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), i.e., the prototype PAH with one six- and one five-membered ring.

(2) We aim to unravel the reaction dynamics of the key RSFR 1,2,3-butatrien-1-yl (H_2CCCCH; i-C_4H_3) with benzene (C_6H_6) accessing the $C_{10}H_9$ PES. This study probes the formation of the *bicyclic naphthalene* molecule ($C_{10}H_8$), i.e., the prototype PAH with two six-membered rings.

(3) We expose the reaction dynamics of key ARs [1- and 2-naphthyl ($C_{10}H_7$)] with vinylacetylene (C_4H_4) accessing the $C_{14}H_{11}$ PES. These studies investigate the synthesis of the *tricyclic anthracene/phenanthrene* molecules ($C_{14}H_{10}$), i.e., prototype PAHs with three six-membered rings.

(4) 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 $C_{13}H_{11}$ PES. These studies investigate the formation of the *tricyclic fluorene/1H-benz[f]indene/1H-benz[e]indene*, i.e., prototype PAHs with two six- and one five-membered ring, as well as of *1H-phenalene* ($C_{13}H_{10}$).

To achieve these goals, we conduct state-of-the-art crossed molecular beam experiments over a wide range of collision energies from 20 to 80 $kJmol^{-1}$ in a hydrocarbon-free, crossed molecular beam machine at The University of Hawaii with ultra-sensitive detection schemes coupled to a universal and rotatable angular resolved time-of-flight mass spectrometric detector with soft and hard electron impact ionization and laser induced fluorescence (LIF) detection. Although crossed beam experiments have been employed for almost five decades, with the exceptions of the crossed beam studies of phenyl with methylacetylene/allene and with vinylacetylene leading to indene and naphthalene, respectively, no bimolecular reaction forming PAHs has been studied experimentally under single collision conditions. Due to the high reactivity of the open shell reactants, crossed molecular beam experiments, in which the reactants are prepared in separate side chambers, present a viable experimental approach. The results of the scattering experiments are combined with *ab initio* calculations (Alexander Mebel) and with flame modeling (William Green). This helps to extract the underlying chemical dynamics, reaction mechanisms, products and intermediates, energetics, branching ratios, and enthalpies of formation of PAHs. This also assists to comment on the vital role of these processes to form distinct PAHs and their isomers in combustion flames. These data are very much required by the combustion chemistry community to understand the formation of PAHs and their hydrogen deficient precursors from the bottom up.

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

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PROGRAM SCOPE

The goal of this project is to develop first-principles, systematic, and size-consistent electronic and vibrational many-body methods, which should ultimately be applicable to solids and molecules of any sizes. The methods must go beyond density-functional theory for electrons or harmonic approximations for vibrations.

For electrons, we will explore new mathematical schemes that dramatically speed up *ab initio* electron correlation calculations, which are otherwise too expensive to apply to solids and large molecules. They may involve approximations in the dimension unique to periodic solid calculations: the reciprocal (k) space. We will develop the logarithm many-body perturbation (MP) and coupled-cluster (CC) methods, in which exponential downsampling in the k space in the Brillouin-zone integration is applied; the hybrid CC/MP method, which uses CC for conduction and valence bands and MP for the rest; and the size-extensive configuration-interaction methods for metals.

For vibrations, we will establish a whole array of diagrammatic thus manifestly size-consistent theories for anharmonic (lattice) vibrations. We will generalize the vibrational self-consistent field (VSCF), vibrational MP, and vibrational CC to solids under periodic boundary conditions and analyze their size dependence. We will implement them and apply them to anharmonic vibrations in solids and large molecules.

FY 2012 HIGHLIGHTS

To understand the principle underlying size-consistent design of electronic and vibrational methods, we must first know why an energy is extensive in the first place, i.e., why the lattice sums of various chemical interactions converge at finite values. We have obtained a semi-rigorous proof of extensivity of energy ("the stability of matter of the second kind") by showing that each of the effective chemical interactions (kinetic, Coulomb, exchange, and correlation) decays faster than the threshold of extensive asymptote in a metal or nonmetal. On this basis, a number of theorems useful for size-consistent design of methods have been derived.

On the basis of the general theories of anharmonic lattice vibrations introduced by us in the previous funding cycle, we have developed diagrammatic and thus manifestly size-consistent versions of VSCF, which we call XVSCF. They are defined as the inverse Dyson equations with Dyson self-energies obtained by the diagrammatic first-order perturbation theory for frequencies and/or geometries. The frequencies and vibrationally averaged geometry of XVSCF converge at those of VSCF in the bulk limit, while XVSCF is many orders of magnitude faster and algorithmically more stable than VSCF.

Theoretical Studies of the Reactions, and the Spectroscopy of Radical Species Relevant to Combustion Reactions and Diagnostics

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PROGRAM SCOPE

We are currently pursuing an ambitious program to accurately represent potential energy surfaces coupled by conical intersections for reactive and/or dissociative systems and for bound systems relevant to combustion. The investigations of reactive/dissociative systems utilize an extension of the method we previously developed to represent coupled bound state surfaces. The coupled bound state surface representations enabled determination of photoelectron spectra when the states of the residual species are coupled by conical intersections. The algorithms produce a coupled diabatic state representation of the adiabatic potential energy surfaces and their couplings and concurrently describe that representation using a matrix of polynomials. They take advantage of symmetry, point group symmetry for bound states, and complete nuclear permutation inversion(CNPI) symmetry for dissociative/reactive systems. The resulting fit representations will enable nonadiabatic dynamics to be performed with unprecedented accuracy.

We are currently studying the quenching of OH(A) by H_2 to produce H_2O(X) +H or OH(X)+H_2, the photodissociation of H_2COH to produce H_2CO+H or H+HCOH, and the photodissociation of phenol to produce H+C_6H_5O. The phenol project requires us to extend our existing algorithm to handle larger molecules, which are comprised of a combination of bound and dissociative parts. This methodology is currently under development, as part of our DOE-sponsored research.

Using the bound state algorithm, we have extended our studies of substitutional isomers of the classic Jahn-Teller molecule methoxy, to include hydroxymethoxy. We are also studying the effect of Jahn-Teller coupling on the spin-orbit interaction in Jahn-Teller molecules, including the propyne cation, $CH_3CCH^{+,}$ and cyclopentadienyl, C_5H_5.

FY 2012 HIGHLIGHTS

One of the highlights of our computational work was the construction of a coupled state representation of the two lowest electronic states of hydroxymethoxy. As a consequence of large amplitude motion of the hydroxyl hydrogen, we found significant differences between the locus and topography of the seam of conical intersections for hydroxymethoxy and the ostensibly similar alkoxy radicals, isopropoxy and ethoxy, studied previously. Interestingly, previous high quality studies of hydroxymethoxy failed to consider the role of conical intersections.

In the first phase of our OH+H_2 work, we have mapped out the locus and determined the local topography of the seam's conical intersection relevant to the electronic quenching process noted above. Several regions of the conical intersection seam not previously described were uncovered.

Dynamics of Activated Molecules

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Funding:	$160,000

PROGRAM SCOPE

The overall goal of this project is to investigate the collisional energy transfer processes that quench highly vibrationally excited molecules in combustion environments. Collisional quenching of activated molecules in the gas phase is in direct competition with chemical reactions and is the most common outcome of collisions for non-radical species. However, the efficiency of the quenching process shows wide variability depending on the identity of the molecular collision partner. We investigate the microscopic mechanisms for energy transfer to identify the relevant molecular features that impact the relaxation process. In our experiments, we prepare highly vibrationally excited molecules under low pressure conditions using pulsed UV excitation followed by rapid radiationless decay. The full energy partitioning of the scattered bath molecules is measured using high resolution transient IR absorption spectroscopy. The nascent appearance and depletion of individual bath states (rotation and vibration) are measured and used to characterize the key pathways. The third energy component is the translational energy, which we determine for individual states by measuring transient Doppler-broadened line profiles. The proposed experiments will focus on two areas of investigation, both involving substantial instrument development. In the first, we will investigate how the rotational energy structure in the bath molecule affects the primary relaxation pathway by measuring the outcome of collisions of HCl and DCl with high energy donors. In the second, we will use saturation spectroscopy to measure how a single initial bath state transforms to the product distribution through collisions. The state-to-state measurement will give insight into the propensity rules that govern collisional quenching. The result will provide detailed information that is needed to develop accurate and predictive models of energy transfer that is ubiquitous in combustion processes.

FY 2012 HIGHLIGHTS

We have successfully constructed an OPO-based transient IR absorption spectrometer for transient IR absorption measurements of HCl, and we have used this instrument to characterize the two energy transfer pathways for collisions of HCl and pyrazine($E=38000$ cm^{-1}). The major pathway leads to HCl ($v=0$) products, and the minor channel leads to ($v=1$) products. The product distributions for HCl and DCl have substantial differences that cannot be attributed to differences in their rotational energy ladders. It appears that strong intermolecular attraction affects the energy transfer in a significant way, and it is likely that vibrational resonances may be important in the relaxation process. We are now using isotopically labeled donors to clarify the role of such resonances. For the state-to-state studies, we have begun construction of a second transient IR absorption spectrometer and performed initial measurements using a quantum cascade laser to saturate individual states of CO_2.

Investigation of Non-Adiabatic Effects in Reactive and Inelastic Collisions of Molecular Combustion Intermediates

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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 which may be difficult to access experimentally. An essential component is the accurate determination of potential energy surfaces (PESs), using multi-reference, configuration-interaction, and coupled-cluster techniques. After fitting the *ab initio* points to obtain global PESs, we treat the dynamics using time-independent (close-coupling) quantum scattering methods. The particular focus of our program is collisions of small polyatomic hydrocarbon radicals (CH_2 and CH_3), in which energy transfer has been little studied up to now.

FY 2012 HIGHLIGHTS

Collisions of the first-excited a^1A_1 state of methylene with He have been studied extensively experimentally at Brookhaven, in the group of Hall and Sears. We have determined PESs for the interaction of CH_2 in both its ground X^3B_1 and the excited *a* state with He, and determined cross sections and rate constants for inelastic scattering, both within a single electronic state and from the *a* to the *X* state. We have also accomplished similar studies of the relaxation of the methyl radical in its ground electronic state. The anisotropy of the PESs, for interaction of these polyatomic species, is more complex than for relaxation of a diatomic radical, and reveals itself in interesting propensities for relaxation within a given so-called *k stack*, where the molecule is rotationally excited or de-excited while the projection of *j* along the figure axis is preserved, and for transitions between different *k* stacks.

In the case of CH_2, the excited state has a pronounced Lewis amphoterism, with a doubly-filled 2*p* orbital in one plane and a vacancy in the other plane. This results in significantly larger cross sections for relaxation of the *a* state as compared to the *X* state. Our calculated overall relaxation rates agree well with the experimental values from Brookhaven, and give confidence to our state-to-state relaxation rate constants, which would be difficult to determine experimentally.

Inter-state relaxation—collision-induced internal conversion—is dominated by weak mixing between the two states due to accidental degeneracies. Recently, we have started to investigate relaxation involving changes in the lowest frequency vibrational modes of CH_2 (the bending mode) and CH_3 (the out-of-plane torsional mode).

Also, to draw a connection with work on combustion modeling, we are now investigating whether the transport properties of the methylene and methyl radicals—the diffusion, viscosity, and heat transfer rates—can be modeled accurately by the simple Lennard-Jones atom-atom potentials which are currently used.

Computer-Aided Construction of Chemical Kinetic Models

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PROGRAM SCOPE

The combustion chemistry of even simple fuels can be extremely complex, involving hundreds or thousands of kinetically significant species. The most reasonable way to deal with this complexity is to use a computer not only to numerically solve the kinetic model, but also to construct the kinetic model in the first place (and also to help with the analysis of the results of the simulations). This project is developing, testing, and disseminating these computer methods, and associated tools and databases, which are gathered together in the open-source RMG software package. Our ultimate goal is to make combustion a predictive science, greatly reducing the need for experimentation when developing new engines and fuels, which will significantly accelerate the innovation cycle in this industry, and help in the discovery of more environmentally-friendly approaches.

FY 2012 HIGHLIGHTS

Making combustion chemistry predictions fast, reliable, and accurate for any fuel and combustion conditions is very challenging. One key challenge is determining the rate coefficients, and several of our journal publications in FY2012 report new rate coefficients for combustion reactions based on quantum mechanical calculations. These calculated rates are used to develop rate estimation rules for similar reactions and incorporate them into the RMG database. It is necessary to accurately account for the effects of pressure on the rates (due to chemical activation/fall-off), and we have automated those calculations and compared different methods used to extract phenomenological rate coefficients k(T,P) from the full master equations. Often the kinetic model predictions are very sensitive to the thermochemistry of small radicals, so we have computed many of these and developed a method to achieve very high accuracy in the computed enthalpies. It is necessary to reliably estimate the thermochemistry of all the molecules involved in the chemical kinetic models; this is particularly tricky for non-planar fused cyclic molecules, but we have made significant progress in algorithms and software for this task. Finally, after one has constructed the chemical kinetic model with all the correct reactions, rate coefficients, and molecular properties, one needs to solve the simulation equations in the experimental geometry. Usually this requires solving a reacting flow simulation accurately. To accomplish this, we have recently developed new software for solving steady and time-dependent one-dimensional or cylindrically symmetric reacting flow simulations, based on a new more accurate operator splitting approach we have invented. The computer predictions are in excellent agreement with many recent experimental measurements by other DOE researchers, and we are now carefully examining the origins of the remaining discrepancies between the simulations and the experiments.

Spectroscopic and Dynamical Studies of Highly Energized Small Polyatomic Molecules

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Funding:	$160,000

PROGRAM SCOPE

The fundamental goal of this program is to develop the experimental techniques, diagnostics, interpretive concepts, spectrum-assignment strategies, and pattern-recognition schemes needed to reveal and understand how large-amplitude motions are encoded in the vibration-rotation energy level structure of small, gas-phase, combustion-relevant polyatomic molecules. We are focusing our efforts on unimolecular isomerization in several prototypical systems, including the HNC ↔ HCN and HCCH ↔ CCH2 isomerization systems. We are developing chirped-pulse millimeter wave (CPmmW) spectroscopy as a technique that can be used in conjunction with Stimulated Emission Pumping (SEP) and the Stark effect to populate and identify molecular states with high excitation in local large-amplitude vibrational modes, which are of key importance in understanding isomerization processes. In addition, we are attempting to demonstrate the capability of CPmmW spectroscopy to determine reaction mechanisms and the structures of molecular fragmentation transition states by measurement of fragment species/vibrational level populations.

FY 2012 HIGHLIGHTS

We have made important advances towards new diagnostics and techniques relevant to highly excited molecules near transition states, the bottlenecks that control kinetics, and the course of chemical processes. First, our comprehensive examination of the *cis-trans* isomerization in S_1 acetylene has led to the development of a universal model-independent spectroscopic diagnostic of transition state energies in systems exhibiting conformational change. We believe it is possible to extend the concept of effective frequency as an indicator of qualitative dynamical changes, previously used for dissociation in diatomics (Birge-Sponer, LeRoy-Bernstein) and the bent-linear transition in quasilinear triatomics (“Dixon dip”), to determine the isomerization barrier height in asymmetric double minimum potentials. Second, the application of CPmmW spectroscopy to pyrolysis and photolysis fragments has proven a powerful tool for the analysis of unimolecular decomposition. The ability to measure vibrational level populations in multiple product species will allow us to extract information about the structures of transition states for fragmentation and photodissociation. Very recently we have realized that bimolecular reactions in a hot pyrolysis tube are crucial for an understanding of the reaction mechanisms and can lead to new chemistry. Of particular interest are the free H-atom mediated reactions, which are our current focus in pyrolysis experiments. Finally, we continue to develop the technological and theoretical tools necessary to continue to break new ground in these frontier research areas.

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

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PROGRAM SCOPE

This project focuses on the development and applications of *ab initio* electronic structure methods and computer codes, exploiting the coupled-cluster (CC) wave function ansatz, which can provide an accurate description of chemical reaction pathways, properties other than energy, and molecular electronic excitations. The goal is to design and apply affordable approaches that enable precise modeling of molecular processes and properties relevant to combustion, catalysis, and photochemistry. Among the most successful methods developed to date are (1) the completely renormalized (CR) CC and equation-of-motion CC (EOMCC) approaches; (2) the local, low-order-scaling, CC methods for larger molecular systems; (3) the active-space CC/EOMCC approaches; and (4) the genuine multi-reference CC (MRCC) theories. The focus is on methods that offer high accuracy, ease of use, and lower computer costs compared to other approaches that aim at similar precision, so that we can study complex molecular problems with dozens or hundreds of atoms, in addition to smaller systems, in a predictive manner. 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 calculation. The active-space CC and EOMCC approaches, their electron-attached and ionized extensions, and the genuine MRCC methods enable practical high-accuracy calculations for a wide variety of closed-shell, open-shell, and strongly correlated electronic states. Our methods can utilize multi-node, multi-core computer architectures; are well suited for automated and parallel implementations; and are available in GAMESS and NWChem.

FY 2012 HIGHLIGHTS

We have merged the active-space and renormalized CC/EOMCC approaches. By examining bond dissociation curves, reaction pathways involving biradical transition states, and singlet-triplet gaps in biradicals, we have shown that the resulting CC(P;Q) methodology provides nearly exact total and relative energies at the fraction of computer costs of high-order CC calculations, competing with the best MRCC theories. We have introduced a low-order-scaling theory combining local higher-level and canonical lower-level approaches, demonstrating its utility in unprecedented CR-CC calculations for cobalt-methyl dissociation in methylcobalamin. We have incorporated the size-intensive modification of our CR-EOMCC(2,3) theory, successfully applied it to spectral shifts induced by chromophore-solvent interactions, in GAMESS, and used it to uncover the existence of the doubly excited state that mediates the multi-photon ionization of azulene. We have helped develop an improved correlation-consistent composite approach for thermodynamic properties and reaction paths in GAMESS, in which CCSD(T) is replaced by our more robust CR-CC(2,3) method. We have developed initial versions of the doubly electron-attached and ionized EOMCC theories with active-space high-order excitations, which provide nearly exact results for biradical electronic spectra. We have used our methods to model the JP-10 fuel initial decomposition phases and photoabsorption spectra of open-shell transition-metal complexes and methylcobalamin.

Developing a Predictive Model for the Chemical Composition of Soot Nanoparticles: Integrating Model and Experiment

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PROGRAM SCOPE

The overall objective of this project is to elucidate the chemistry of how soot and its precursors are formed in combustion environments. Multiscale computational studies in conjunction with state-of-the-art experiments are the distinguishing characteristics of this unique interdisciplinary effort. The modeling effort is conducted at the University of Michigan by Prof. A. Violi. The experimental team includes Dr. N. Hansen and H. Michelsen at Sandia National Labs' Combustion Research Facility and Dr. K. Wilson at Lawrence Berkeley National Lab's Advanced Light Source. The new chemical insights into molecular-growth chemistry in flames obtained from these studies provide guidance and benchmarks for further developments of soot-formation models with detailed chemical understanding and predictive capabilities. The results have the potential to fundamentally transform our understanding of early soot-formation processes in combustion environments and can help establish a scientific foundation of sufficient depth that will facilitate simulation of combustion processes in existing and proposed engine designs.

FY 2012 HIGHLIGHTS

We have investigated the growth of polycyclic aromatic hydrocarbons (PAHs), using molecular dynamics simulations, with the specific aim of assessing the role of PAHs in the transition from small aromatics to macromolecular structures. Analyses of systems composed of thousands of homo-molecular and hetero-molecular molecules highlighted the importance of molecular mass, morphology, and temperature on the nucleation process. At temperatures higher than 1000 K, small clusters of are not stable enough to accommodate the further growth into larger particles. This result raises doubts on the ability of these molecules to become soot nuclei. Aromatics with attached aliphatic chains show considerably faster nucleation rates than the corresponding PAHs of similar mass without any chain. These results can lead to the development of a more complex model to describe the physical nucleation of PAH.

In order to validate and guide the modeling development, we have designed an opposed-flow flame system to investigate the chemical composition of non-premixed flames using in situ flame-sampling molecular-beam mass spectrometry with synchrotron-generated tunable vacuum-ultraviolet light as an ionization source. We measured quantitative mole-fraction profiles as a function of the distance from the fuel outlet for the major species and several intermediates for three low-pressure (30–50 Torr), non-premixed, opposed-flow acetylene flames. A comparison between experimental and model results demonstrates excellent agreement for major species with more modest agreement among minor species.

Publication: "Studies of laminar opposed-flow diffusion flames of acetylene at low-pressures with photoionization mass spectrometry," S. A. Skeen, B. Yang, H. A. Michelsen, J. A. Miller, A. Violi, N. Hansen, Proc. Combust. Inst. (2013), in press.

The Effects of Oxygenated Fuel Compound Structure on Combustion and Pollutant Reaction Chemistry

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PROGRAM SCOPE

The increased use of alternative fuels, including biofuels, synfuels and sources of alternative fossil fuels, presents an exciting opportunity to improve combustion performance while simultaneously reducing greenhouse gases and pollutant emissions. Realization of this potential, however, requires more complete understanding of the fundamental reaction chemistry at conditions relevant to advanced combustion systems, i.e., moderate temperatures and elevated pressures. This study focuses on understanding the elementary combustion chemistry of hydrocarbon and oxygenated hydrocarbon compounds through comprehensive experimental and modeling efforts. The effects of composition and chemical structure are examined through ignition studies. Ignition delay time measurements are used to quantify the effects of composition and structure on reaction rates. Gas chromatography of stable intermediate species is used to interrogate the effects on fuel oxidation pathways and on formation of sentinel species for soot production. The outcomes of this work provide direct measurements of the reaction pathways important in combustion of reference fuel compounds at conditions directly relevant to modern combustion systems.

FY 2012 HIGHLIGHTS

In the past year, fundamental studies of several important fuel species have been completed, including n-butanol, methyltrans3hexenoate, and blends of n-butanol and n-heptane. The study of n-butanol highlights how global reactivity of n-butanol is well understood, yet key intermediate reaction pathways are not as well predicted. As we might expect, global reactivity does not necessarily equate to quantitative understanding of the rates of production of important intermediate and product species. And only a combination of global and detailed reaction parameters, like ignition delay time and corresponding species time histories, can identify divergence in the reaction chemistry. In the ignition study of the methyltrans3hexenoate, we learned that the reaction chemistry of unsaturated methyl esters lags that of the saturated ester counterparts. This is particularly relevant as over 90% (mass basis) of biodiesel fuels are unsaturated ester compounds. In the study of the fuel blend of n-heptane and n-butanol, we discovered synergistic interactions between the fuels where the presence of the n-butanol altered the fundamental reaction pathways of the n-heptane. Such fuel component interactions are neither well documented nor well understood, and are critical to the fueling strategies of the future where more diverse fuel blends are inevitable.

Variational Transition State Theory

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PROGRAM SCOPE

This project involves the development of variational transition state theory (VTST) including optimized multidimensional tunneling (OMT) contributions and its application 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 (1) developing and applying new methods of electronic structure calculations for the input potential energy surface, which is typically an implicit surface defined by a level of electronic structure theory; (2) methods to interface reaction-path and reaction-swath dynamics calculations with electronic structure theory; and (3) 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 application of VTST to gas-phase reactions is carried out by direct dynamics, and it 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 2012 HIGHLIGHTS

Multi-structural canonical variational-transition-state theory with multidimensional tunneling (MS-CVT/MT) was employed to calculate thermal rate constants for several combustion reactions over a temperature range from below room temperature to above 3000 K. The internal rotations in some of the transition states were found to be highly anharmonic and strongly coupled to each other, and they generate multiple structures (conformations) whose contributions were included in the partition functions. The rate constants obtained from the best MS-CVT/MT calculations carried out in this study, which include variational effects, torsional anharmonicty, and multidimensional, are recommended for future refinement of the kinetic model for methanol combustion. We also proposed a new formulation of variational transition state theory, called multi-path variational transition state theory. We developed a portable Fortran program package, MSTor, that calculates partition functions and thermodynamic functions of complex molecules involving multiple torsional motions by the MS-T method; and we deposited it in the *Computer Physics Communications* Program Library. In summary, we have developed powerful new methods for calculating thermodynamic quantities and rate constants for complex molecules; and we have used them for several applications relevant to combustion.

Hydrocarbon Radical Thermochemistry: Gas-Phase Ion Chemistry Studies

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PROGRAM SCOPE

Gas-phase ion chemistry and mass spectrometry techniques are employed to determine the energetics of hydrocarbon radicals that are important in combustion processes and to investigate the dynamics of ion–molecule reactions. Tandem mass spectrometry is used to measure the activation of endoergic ion-molecule reactions as a function of kinetic energy. Modeling the measured reaction cross sections using statistical rate theory and empirical reaction models allows extraction of reaction threshold energies. These threshold energies yield relative gas-phase acidities, proton affinities, or absolute dissociation energies, which may then be used in thermochemical cycles to derive neutral R–H bond dissociation enthalpies and radical enthalpies of formation. The reactive systems employed in these studies include endoergic bimolecular proton transfer reactions, hydrogen-atom transfer reactions, and collision-induced dissociation of heterodimer complex anions. Electronic structure calculations are used to evaluate the possibility of potential energy barriers or dynamical constrictions along the reaction path, and as input for RRKM and phase space theory calculations. These investigations provide thermochemical data on hydrocarbon radicals that are important inputs for chemical kinetics and mechanistic modeling of combustion systems.

FY 2012 HIGHLIGHTS

We completed work on the threshold collision-induced dissociation of peroxyformate anion, $HC(O)OO^-$. The energy threshold for the loss of O atom from the peroxyformate anion to form formate anion, HCO_2^-, was measured. Using the measured threshold energy and recent measurements of the gas-phase acidity of HCO_3H, we can obtain the first experimental values for the enthalpies of formation of the neutral peroxyformic acid, HCO_3H, and neutral peroxyformyl radical, HC(O)OO, which is an intermediate in the oxidation of the HCO radical. We are continuing work on other oxygen containing hydrocarbon radicals of combustion interest, including in combustion of biofuels.

Quantum Dynamics of Elementary Chemical Reactions

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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 2012 HIGHLIGHTS

We have made major progress towards a better understanding of a prototypical complex-forming reaction, namely $HO + CO \rightarrow H + CO_2$, which represents the major CO oxidation and heat release step in hydrocarbon combustion. We have recently reported the first chemically accurate potential energy surface for this system and carried out both quasi-classical trajectory and quantum wave packet studies of its dynamics. The results indicated significant improvements in experiment-theory agreement although many problems remain.

We have also spearheaded the investigation of mode selectivity in chemical reactions. To this end, we have recently reported the first ab initio based global potential energy surface for the $F + H_2O \rightarrow HF + OH$ reaction and carried out both quasi-classical trajectory and quantum wave packet studies of the reaction dynamics. It was found that a deep pre-reaction complex is responsible for a substantial enhancement of the reactivity near the threshold, due apparently to stereodynamics. Further investigations revealed that the vibrational energy is more effective in promoting the reaction than translational energy. Since this reaction has an earlier barrier, this observation raises questions about the general applicability of the venerable Polanyi's rules.

Dynamics of Radical Reactions in Biodiesel Combustion

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

PROGRAM SCOPE

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 peroxy radical chemistry from compounds that are models for biodiesel ignition. This includes chain terminating and chain-propagating reactions of peroxy radicals. In addition, the research will (1) include rigorous treatments of tunneling effects, (2) quantify the effect of chemically activated processes, and (3) synthesize the results into structure-activity relations (SARs).

FY 2012 HIGHLIGHTS

Biodiesel fuel is composed largely of fatty acid methyl esters (FAMEs) that possess double bonds in cis configurations. By contrast, gaseous alkenes studied in combustion are mostly trans. Hydrogen abstraction from alkenes often creates allylic radicals, whose fate may depend on whether they are cis or trans. Previous work neglected the potential for cis-trans isomerization of these allylic radicals. Our work showed that chemically activated and thermal cis-trans isomerization is fast. This means that modeling studies of the combustion of FAMEs needs to include trans-allylic radicals, and modeling studies of the combustion of trans-alkenes needs to include cis-allylic radicals. Chemically activated cis-trans isomerization is highly dependent on the quantum chemical method used to generate data to compute sums and densities of states, and also on the treatment of anharmonicity and torsional modes.

We have carried out quantum calculations on the reactions of the *cis*- and *trans*-but-2-en-1-peroxy radical formed by O_2 addition to C_1 of 2-butenyl radical:

$$[CH_3CH{=}CHCH_2\bullet \leftrightarrow CH_3CH\bullet CH{=}CH_2] + O_2 \rightarrow CH_3CH{=}CHCH_2OO\bullet \quad (1)$$

Only the cis isomer of the product of this reaction has the potential to undergo an H-shift reaction that could lead to chain branching. The results indicate that loss of O_2 (reaction -1) is ~3 kcal/mol favored over the H-shift reaction. Given that reaction (-1) has a higher Arrhenius pre-exponential term than H-shift, loss of O_2 will be favored under all conditions.

The oxidation mechanism of methyl butanoate (MB) has 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 include all four peroxy radicals formed subsequent to H-atom abstraction from MB. Reactions treated include H-shift and HO_2 elimination of ROO•, and several unimolecular reactions of QOOH.

Kinetics and Product Channel Studies in Combustion Chemistry

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Funding: $90,000

PROGRAM SCOPE

The radical-radical and radical-molecule chemistry of small nitrogen-containing compounds, especially NO and NO_2, play a crucial role in combustion chemistry, partly because of the problem of NO_x pollutant emissions in the combustion of fossil fuels. Knowledge of kinetic parameters of elementary reactions is an important step towards development of reliable kinetic models of overall combustion processes. Our research program is devoted to kinetics studies of elementary reactions relevant to NO_x chemistry. Our primary experimental technique is laser flash photolysis/infrared diode laser absorption spectroscopy.

We also use modern ab initio computational techniques in some cases to investigate the potential energy surfaces of these reactions.

FY 2012 HIGHLIGHTS

Recent work has concentrated on three projects:

(1) O + ICN Reaction. This reaction is potentially important because ICN is a common photolytic precursor for CN radicals, which are important in combustion environments. We used a relative rate technique to measure the total rate constant of this reaction, and find that it is very slow, ranging from $(3.7\pm1.0 – 26.2\pm4.0) \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} over the pressure range 1.5-9.5 Torr. No NCO product was detected, suggesting ICNO adduct as the sole product channel. This conclusion is supported by ab initio calculations.

(2) CN + HCNO Reaction. Fulminic acid, HCNO, is produced in the oxidation of acetylene in the presence of NO. Recently published ab initio calculations disagreed with previous experimental work in our laboratory regarding the dominant product channel. We have therefore reinvestigated this reaction using several new approaches, including direct detection of HCN and HCCN products. Our results strongly indicate that the conclusion reached in earlier experimental work was accurate (i.e., that HCCN + NO product formation dominates).

(3) C_2H + NO Reaction. We are currently investigating the product channels of this reaction. The major channel is HCN + CO, as predicted by previous ab initio calculations. We did find evidence, however, for a previously unknown minor product channel, HCO + CN, with a ~20% yield.

Spectroscopic Detection, Characterization and Dynamics of Free Radicals Relevant to Combustion Processes

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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 peroxies 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 2012 HIGHLIGHTS

Hydroxy peroxy radicals, HOROO where R is an organic group, are important intermediates in the combustion of alcohol containing fuels. They can also be formed in oxidation of unsaturated organic compounds. We have recently begun investigating the spectroscopy of hydroxyl peroxy radicals, with the simplest species, hydroxyl ethyl peroxy and hydroxyl propyl peroxy. In the past year, we have observed and analyzed the spectrum of hydroxyl propyl peroxy after performing similar work on hydroxyl ethyl peroxy the year prior. In addition to the spectral analysis and characterization, we have discovered a dynamical effect in the excited electronic state of hydroxyl ethyl peroxy which leads to a dramatic decrease in its lifetime. The cause of the decrease is attributed to an isomerization from the hydroxyl ethyl peroxy isomer, HOC_2H_4OO, to the ethoxy peroxide isomer, OC_2H_4OOH. The reaction is analogous to the isomerization of alkyl peroxy radicals, ROO, to form QOOH, long postulated to be of importance in low temperature combustion.

Dynamical Analysis of Highly Excited Spectra

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PROGRAM SCOPE

Highly excited vibration-rotation dynamics of small molecular species, including those approaching the threshold of reaction, are crucial to understanding fundamental processes in combustion. The goal of our program is to develop theoretical tools to analyze spectra and dynamics of these highly excited systems. A constant theme is the use of effective spectroscopic fitting Hamiltonians to make the link between experimental data and theoretical dynamical analysis. We emphasize, particularly, the role of bifurcations and the birth of new modes in bifurcations from the low energy normal modes. A new focus has been systems approaching and undergoing chemical reactivity, including 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. Our current research is pursuing two main directions. The first is polyad-breaking generalized effective Hamiltonians, especially for isomerizing systems, with a new emphasis on the fundamental meaning of the abstract effective Hamiltonian in relation to the real Hamiltonian of the physical molecule. The second emphasis is bifurcation analysis of spectroscopic Hamiltonians, to find new modes that come into existence in high-energy systems, with a recent emphasis on full rotation-vibration dynamics. In both of these focuses of inquiry, we are investigating molecular species of crucial importance in combustion, in particular, the acetylene-vinylidene system, and the hydroperoxyl system (HO_2).

Intermolecular Interactions of Hydroxyl Radicals on Reactive Potential Energy Surfaces

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PROGRAM SCOPE

Hydroxyl radicals are important in combustion environments, where they are often detected by laser-induced fluorescence on the $A^2\Sigma^+$–$X^2\Pi$ band system. However, collision partners known to quench electronically excited OH $A^2\Sigma^+$ radicals are ubiquitous in these environments. Despite extensive kinetic measurements of the rates for collisional quenching, fundamental questions remain regarding the fate of the collisionally quenched molecules and the *mechanism* by which these nonadiabatic processes occur. The experimental work carried out under DOE-BES funding in the Lester laboratory is aimed at understanding the fundamental chemical dynamics governing quenching of OH $A^2\Sigma^+$ by molecular partners (M = H_2, O_2, N_2, CO, CO_2, H_2O) of significance in combustion environments.

FY 2012 HIGHLIGHTS

Recently, a new quantum state-selective ionization scheme has been developed for OH radicals using UV+VUV resonant ionization. The UV photon prepares the long-lived and well-characterized $A^2\Sigma^+$ valence state as the resonant intermediate state and a subsequent VUV photon (10.5 eV) accesses autoionizing ($A^3\Pi$) *n*d Rydberg states. This sensitive ionization scheme for OH radicals is applicable to velocity-map ion imaging of fundamental reaction, photodissociation, and inelastic collision dynamics.

In addition, the outcomes following collisional quenching of electronically excited OH $A^2\Sigma^+$ by O_2 and CO have been examined in a combined experimental and theoretical study. The atomic H- and O-atom products from reactive quenching were probed using two-photon laser-induced fluorescence to obtain the relative yields of these products. The experimental product branching ratios show that the O-atom producing pathways are the dominant outcomes of quenching: the OH $A^2\Sigma^+ + O_2 \rightarrow O + HO_2$ channel accounts for 48(3)% of products and the OH $A^2\Sigma^+ + CO \rightarrow O + HCO$ channel yields 76(5)% of products. Theoretical studies also characterized the properties of energy minimized conical intersections in regions of strong nonadiabatic coupling accessible from the OH $A^2\Sigma^+$ + CO asymptote. Energy minimized points were located on a seam of conical intersection from the OH $A^2\Sigma^+$ + CO asymptote to a conical intersection with an extended OH bond length and the H-side of OH pointing towards CO in a bent configuration. This region, exoergic with respect to the reaction asymptote, is likely to be the origin of the dominant O + HCO product channel.

Advanced Nonlinear Optical Methods for Quantitative Measurements in Flames

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Funding:	$120,000

PROGRAM SCOPE

The overall objective of the research program is the development of new nonlinear optical diagnostic techniques for quantitative measurements in flames. We are presently investigating high-spectral-resolution, two-color polarization spectroscopy (PS) for minor species measurements and femtosecond (fs) coherent anti-Stokes Raman scattering (CARS) for high-data-rate measurements of temperature and major species concentrations. We are exploring the potential of these techniques by performing measurements in well-characterized flames and in gas cells. We also developed a new nanosecond CARS technique that enables simultaneous detection of vibrational and pure rotational CARS spectra using a standard three-beam CARS arrangement.

For the PS experiments, we use high-spectral-resolution, injection-seeded optical parametric generation (OPG) systems, and pulsed-dye-amplifiers (PDAs) for these measurements to enable more rigorous comparison of theory and experiment. We have developed a new experimental apparatus for the featuring OPGs injections-seeded with DFB diode lasers at 1320 nm and 772 nm with signal outputs at 486 nm and 656 nm, respectively. The signals beams from the OPGs are amplified using PDAs, and the 486-nm beam is then frequency-doubled to 243 nm for two-photon excitation of the 1S-2S resonance. The 656-nm beam is used to probe the 2S-3P transition. Polarization spectroscopy is performed on the laser-pumped population of the 2S level using a circularly polarized 656-nm pump beam and a linearly polarized 656-nm probe beam. We are also investigating the physics of this process by direct numerical integration (DNI) of the time-dependent density matrix equations that describe the resonant interaction. We performed a series of experiments on atomic hydrogen and have now reconfigured the system with a 230-nm two-photon pump beam and a 480-nm single-photon probe beams for measurements of carbon monoxide.

FY 2012 HIGHLIGHTS

We are exploring the potential of using ultrafast laser systems for high-data-rate measurements in flames. We recently used a Coherent ultrafast laser system to perform single-shot fs CARS temperature measurements at a data rate of 5 kHz. We investigated the use of polarization suppression of the nonresonant background in single-pulse temperature measurements. We are currently performing 5 kHz temperature measurements in hydrogen diffusion flames with a buoyant instability, and are installing a co-flow and chimney apparatus for measurements in confined jet diffusion flames. We will explore the potential for single-shot concentration measurements in these flames. Lastly, we have developed a new scheme for simultaneous generation and detection of pure rotational and vibrational N2 CARS using two 532-nm pump beams and a 607-nm dye laser beam. In the future, we plan to introduce a dual-pump CARS variant of the technique for sensitive detection of three or more species along with the temperature measurement from both pure rotational and vibrational CARS.

Isomer-Specific Spectroscopy and Isomerization in Aromatic Fuel

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PROGRAM SCOPE

Under fuel-rich conditions, reactions that lead toward soot formation occur, with aromatic molecules and resonance-stabilized radicals playing key roles as intermediates. Key objectives of this research program are to develop and utilize laser-based methods to characterize the spectroscopy and isomerization dynamics of conformational and structural isomers of aromatic derivatives and resonance-stabilized free radicals that play a role in soot formation. We are also characterizing the spectroscopy of model lignin compounds, with an eye towards improving plants as a source of biofuels. Lignin is an aromatic-rich biopolymer that gives plant cell walls structural integrity and encases the polysaccharides that must be extracted for biofuel production. We are studying the spectroscopy of the aromatic sub-units themselves and of larger oligomers that incorporate the diverse chemical linkages characteristic of lignin. Double-resonance laser spectroscopies are being used to record single-conformation IR and UV spectra of the molecules and radicals free from interference from one another. Populations of the isomers are determined, where possible, using population transfer or infrared ion-gain spectroscopy specially designed for the purpose.

FY 2012 HIGHLIGHTS

We have recorded CH stretch infrared spectra under jet-cooled conditions of a series of resonance-stabilized radicals that are intermediates along pathways to PAH formation, including phenylallyl ($C_6H_5\text{-}\dot{C}H\text{-}CH{=}CH_2$), benzylallenyl $C_6H_5\text{-}\dot{C}H\text{-}CH{=}C{=}CH_2$), inden-2-yl methyl, 1,2,3-trihydronaphthyl and α–methylbenzyl radicals. Single-conformation IR and UV spectra of model β-O-4 and β–β dimers have revealed striking differences in rigidity between these two chemical linkages. We are presently exploring the unique UV spectra of a series of model lignin-like compounds that build up to sinapoyl malate, the molecule responsible for protecting the plant from harmful UV radiation, a kind of “sunscreen” for plants.

Detailed Studies of Hydrocarbon Radicals: C_2H Dissociation Dynamics

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Funding:	$142,000

PROGRAM SCOPE

Excited state properties and dynamics of C_2H are examined. This species is central to hydrocarbon chemistry; it also serves as a good prototype for detailed examination of important properties and phenomena: electronic states, nonadiabatic transitions, and intramolecular and dissociation dynamics. It offers experimental parent and product state resolution, and it is tractable at a reasonably high level of theory. The first goal is unambiguous: accurate determination of the UV absorption spectrum and comparison with theoretical calculations.

FY 2012 HIGHLIGHTS

A large theory paper (PCCP, invited) was published detailing geometric phases that arise through conical intersections. Experimentally, to establish the 193-nm photodissociation efficiency of parent C_2H_2, a depletion approach was used in which a parent mass peak is monitored with $h\nu_{193}$ alternately on and off. No signal was observed with C_2H_2, so the system was checked using H_2S. Huge (> 30%) depletion was recorded right away. Even with increased fluence, C_2H_2 depletion was barely detectable. With high fluence, C_2H is photodissociated efficiently. This showed that σ_{193} is an order of magnitude smaller for expansion-cooled than room temperature C_2H_2. This is attributed to enhancement of σ_{193} with bending excitation. It is unlikely that rotation accounts for the temperature dependence.

This small cross section can be overcome, e.g., CF_3C_2H precursor. However, it is necessary to establish the UV spectrum of C_2H with good accuracy, as it will be compared to theory. This can be achieved by embedding C_2H_2 in a matrix and photolyzing it, i.e., countering a small cross section by large optical depth. C_2H_2 is transparent in the C_2H region of interest, and the CO_2 matrix is transparent at 193 nm ($\sigma < 10^{-23}$ cm^2) and can be used at 80-90 K. C_2H is identified through it's $A \leftarrow X$ infrared features. The CO_2 matrix is transparent at most strong $A \leftarrow X$ frequencies, and C_2H $A \leftarrow X$ absorptions are separated from C_2H_2 combination bands. The apparatus has been tested using FTIR and TOF mass spectroscopy (200 kHz repetition frequency). Molecules will be deposited at 80-90 K, and C_2H_2 will be photodissociated at 193 nm via its weak absorption. The H atom will not react with CO_2 (forming OH + CO), as the maximum translational energy is ~ 6000 cm^{-1}, well below the entrance barrier. The goal is to prepare enough C_2H to enable its IR and UV spectra to be recorded with good S/N. The small 193-nm absorption cross section of low temperature C_2H_2 requires care to avoid efficient dissociation of the C_2H product, i.e., keep fluence low and live with small $\sigma_{193}(C_2H_2)$. Importantly, C_2H will be identified through its IR features. Correlation of the IR and UV features will establish unambiguously the UV absorbing species.

Photoinitiated Reactions of Radicals and Diradicals in Molecular Beams

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Funding:	$140,000

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 for which multiple pathways including molecular rearrangements compete, 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. The detailed measurements on simple systems will serve as benchmarks for a homologous series. By using the imaging technique to detect photofragments and photoelectrons, information on the participating states, their interactions, and their manifestations in product state distributions are obtained.

FY 2012 HIGHLIGHTS

In order to determine product state distributions in photoinitiated dissociation of combustion-relevant radicals with vibrational resolution and infer mechanisms, the time-of-flight detection in our experimental arrangement was replaced with an imaging arrangement designed specifically to achieve sliced velocity map imaging of H-photofragments with comparable resolution to that obtained by reconstructed velocity map images. The ion-optical system has been carefully designed to allow for high kinetic energy resolution for atomic hydrogen fragments over several eV dynamic-range. This was achieved by introduction of an additional electrostatic lens in the drift region and careful computer optimization of focusing conditions. The first implementation of the new arrangement was to re-examine the overtone-induced vibrational predissociation of the hydroxymethyl radical, with special emphasis on the relative roles of direct dissociation, $CH_2OH \rightarrow CH_2O + H$, and dissociation following $CH_2OH \leftrightarrow CH_3O$ isomerization. We observed the production of H atoms in CH_2OH and CD_2OH upon excitation to $4\nu_1$ (OH stretch) and analyzed two absorption bands in this region. From the H fragment kinetic energy distributions, we obtained energy distributions of CH_2O co-fragments. From the analysis of the kinetic energy distributions obtained by detecting H and D fragments from CH_2OH and CD_2OH, we were able to identify that the main channel was direct dissociation, but isomerization to methoxy took place as well. We combined the experimental studies with collaborative theoretical investigations. Electronic structure calculations gave accurate barrier heights, bond dissociation energies, and vibrational level energies. This allowed us to propose a dissociation mechanism and explore the role of isomerization and the possible influence of higher electronic states. These studies have now been expanded to include dissociation from excited Rydberg states and production of CH_2O and HCOH products.

Theoretical Modeling of Spin-Forbidden Channels in Combustion Reactions

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Funding:	$125,000

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 2012 HIGHLIGHTS

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 (PESs). We also continued to develop computational methods for modeling electronic structure and spectroscopy of open-shell species. In 2011-2012, the DOE support has been acknowledged in six publications.

Spectroscopy and Kinetics of Combustion Gases at High Temperatures

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Funding:	$160,000

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 will focus on the study of oxygenate species, particularly the small ketones and aldehydes (e.g., acetaldehyde, propanal, propenal, 2-butanone, and 3-pentanone) and their reactions.

This combination of spectroscopic and kinetics studies provides a strong, and needed, database useful in 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 2012 HIGHLIGHTS

Species currently being investigated in the spectroscopic portion of the research include carbon monoxide (CO) in the IR (near 4.6 μm), formaldehyde (CH_2O) and acetaldehyde (CH_3CHO) in the UV (near 305 nm) and in the IR (near 3.4 μm), and ketones in the UV (near 305 nm). Tunable laser absorption is also used to acquire species time-histories of CH_3 (216 nm), OH (306 nm), H_2O (2.5 μm), CO_2 (2.7 μm), CH_4 (3.4 mm), and C_2H_4 (10.5 μm) in support of the accompanying kinetics studies.

In parallel with these spectroscopic studies, kinetics research has advanced on several fronts. The OH diagnostic has been used to measure the rate constants for the reaction of OH with the isomers of butanol: 1-butanol, 2-butanol, iso-butanol, and tert-butanol. The CO, C_2H_4, and UV ketone diagnostics have been used to provide improved measurements of the decomposition rate constants for acetone and 2-butanone and to provide a comprehensive database of species time-histories for ketone reaction mechanism validation.

Quantum Chemistry of Radicals and Reactive Intermediates

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PROGRAM SCOPE

Our work deals with several areas in the field of theoretical chemical physics. We develop quantum-mechanical methods and other numerical algorithms, and focus our work on problems that are relevant to the study of spectroscopy, unstable molecules and their reactivity (including combustion), as well as processes that occur in the atmosphere and in the interstellar medium. Specifically, work supported by the Department of Energy includes (1) the development and application of very high-accuracy methods for the calculation of thermochemistry (heats of formation, bond energies, and so forth) for small- to medium-sized molecules; (2) a study of molecular ionization that includes both photoelectron spectra and what are known as photo-ion efficiency curves that are targeted towards helping to better understand studies carried out by collaborators at the Synchrotron facility at Lawrence Berkeley Laboratory; and (3) a somewhat new (in implementation only) semi-classical approach for the calculation of molecular reaction rates that shows great promise.

FY 2012 HIGHLIGHTS

We solved the problem of reaction mechanism and chemical kinetics of the HO + CO reaction. We found that quantum mechanical tunneling is very important. Work on the self-reaction of two hydroxyl radicals will be published soon. The calculation of thermochemistry for key chemical species is in progress.

Development of Kinetics for Soot Oxidation at High Pressures Under Fuel-Lean Conditions

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Funding:	$162,000

PROGRAM SCOPE

This project is a joint effort between the University of Utah (UU) and Pennsylvania State University (Penn State). The focus of the proposed research is to develop kinetic models for soot oxidation with the hope of developing a validated, predictive, multi-scale, combustion model to optimize the design and operation of evolving fuels in advanced engines for transportation applications. The work focuses on the relatively unstudied area of the fundamental mechanism for soot oxidation. The objectives include understanding of the kinetics of soot oxidation by O_2 under high pressure which requires (1) development of intrinsic kinetics for the surface oxidation, which takes into account the dependence of reactivity upon nanostructure; (2) evolution of nanostructure and its impact upon oxidation rate; and (3) inclusion of internal surface area development and possible fragmentation resulting from pore development and/or surface oxidation. These objectives will be explored for a variety of pure fuel components and surrogate fuels.

FY 2012 HIGHLIGHTS

At this time, experiments have been conducted in a Thermogravimetric Analyzer (TGA) using pure n-dodecane and m-xylene and a mixture of the two representing a simple jet fuel surrogate. In addition, n-dodecane with the addition of butanol, an oxygenated diesel surrogate, and pure butanol have been studied. Soot was generated in a flat-flame, premixed burner under heavily-sooting conditions and captured on a water-cooled stabilization plate which was located 5-cm above the burner surface. The collected soot was crushed into a powder and oxidized using a Cahn TherMax 500 high pressure TGA. An inert material was used in all the tests to minimize thermal and mass transfer effects by decreasing the stagnant region between the top surface of the soot and the entrance of the crucible. Experiments were performed with 10 mg of sample and volumetric flow rates of 1 L/min. Kinetic parameters have been obtained as a function of pressure and oxygen concentration. It appears as though the order of the rate equation for the oxygen concentration was approximately one. Corrections to the data were needed under pressurized conditions (1 versus 10 atm), and a program was developed to account for this. Pressure did not appear to change kinetic parameters. The kinetic parameters obtained for the butanol and butanol/dodecane mix suggested that the oxidation rate was faster for these fuels as compared to the other fuels studied. In fact, the m-xylene, n-dodecane, and the mixture of these two components had similar rate parameters.

Initial analyses of nanostructure for the oxidized soot samples (50%) suggests differences based on fuel and pressure. These results will be further investigated.

Universal and State-Resolved Imaging Studies of Chemical Dynamics

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PROGRAM SCOPE

The focus of this program is on combining universal ion imaging probes providing global insight, with high-resolution state-resolved probes providing quantum mechanical detail, to develop a molecular-level understanding of chemical phenomena. Particular emphasis is placed upon elementary reactions important in understanding and predicting combustion chemistry. This research is conducted using state-of-the-art molecular beam machines, photodissociation, reactive scattering, and vacuum ultraviolet lasers in conjunction with ion imaging technqiues. An ongoing parallel effort is made to develop new tools and experimental methods with which to achieve these goals.

FY 2012 HIGHLIGHTS

Isomer-specific detection and imaging via “semi-soft” strong-field ionization: The use of “soft” vacuum ultraviolet photoionization to achieve universal but selective detection of reaction products and photofragments began at the Chemical Dynamics Beamline at the Advanced Light Source in the mid-nineties and has had a profound impact on combustion chemistry. It was with the recognition that the full shape of the photoionization efficiency (PIE) curves could be used to identify complex mixtures of isomers in flame studies and kinetics experiments that the power of this approach became clear. Non-resonant ionization by relatively high peak power femtosecond lasers has parallels to tunable VUV photoionization, in that the power needed to saturate the ionization closely tracks the ionization energy of the subject molecule. Unfortunately, our investigations have shown that although one can tune through an effective photoionization efficiency spectrum by tuning the laser power in a manner analogous to the VUV PIE curves, the resulting spectra lack the sharp features and characteristic signatures that are typical of VUV PIE curves. However, one significant difference is that molecules undergo only modest fragmentation upon ionization in the laser field and this fragmentation is very characteristic for each molecule—even distinct for different isomers. By recording the individual spectra under well-defined conditions, we can fit the mixture to determine its composition quite accurately. We believe this will have a substantial impact on combustion diagnostics, as the ability to probe flame chemistry with isomer selectivity will be extended beyond synchrotron beamlines where access and beamtime may be restricted.

Dissociation Pathways and Vibrational Dynamics in Excited Molecules and Complexes

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Sr. Investigator(s):	
Students:	0 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding:	$155,000

PROGRAM SCOPE

Experimental studies of the dissociation of selectively excited molecules probe fundamental aspects of chemical reactivity and molecular decomposition, and understanding excited-state decomposition dynamics presents both experimental and theoretical challenges. Photoexcitation of molecules from selectively prepared vibrational states is a proven means of studying electronically excited molecules and, in favorable cases, of controlling their dissociation pathways. This double resonance scheme, vibrationally mediated photodissociation, has uncovered new vibrational spectroscopy, determined bond strengths with high accuracy, altered excited state dissociation pathways, and revealed properties and couplings in electronically excited states. Many practically important processes, such as excited state decomposition and bimolecular reaction, 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 is a systematic study of the photodissociation of vibrationally excited molecules and of their complexes with various adducts. This research applies vibrationally mediated photodissociation to a series of related molecules to determine the influence of vibrational excitation on their decomposition pathways. Previous studies of the dissociation of ammonia and phenol have shown that vibrational excitation can steer molecules along an adiabatic path to form excited-state products at the expense of ground-state products. The studies described here introduce new possibilities by extending that approach to other molecules and to their complexes. In these experiments, a pulse of infrared laser light prepares vibrationally excited molecules and a pulse of ultraviolet laser light transfers them to an electronically excited state. A third laser pulse, in conjunction with an ion-imaging apparatus, interrogates the dissociation fragments to determine the identity of the products and the distribution of the available energy among their different degrees-of-freedom.

FY 2012 HIGHLIGHTS

The primary highlight of the past year has been the completion and publication of two studies on the vibrational predissociation of the ammonia dimer and trimer. We have determined the dissociation energy of both the dimer (660±20 cm^{-1}) and the cyclic trimer (1750±50 cm^{-1}) while also performing new spectroscopy on the ammonia molecule. The ion-imaging studies provide new insights into the dynamics of the dissociation of the dimer as well and reveal the correlation between the vibrational states populated in the dissociation products.

Computational and Experimental Study of Laminar Flames

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Principal Investigator:	Smooke, Mitchell
Sr. Investigator(s):	Long, Marshall, Yale University
Students:	1 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$237,000

PROGRAM SCOPE

Our research has centered on an investigation of the effects of complex chemistry and detailed transport on the structure and extinction of hydrocarbon flames in coflowing axisymmetric configurations. We have pursued both computational and experimental aspects of the research in parallel. The computational work has focused on the application of accurate and efficient numerical methods for the solution of the boundary value problems describing the various reacting systems.

FY 2012 HIGHLIGHTS

Detailed experimental measurements were performed on axisymmetric coflow flames using two-dimensional imaging techniques. Spontaneous Raman scattering and laser-induced fluorescence were used to measure the temperature, and major and minor species profiles. Laser-induced incandescence (LII) has been used to measure soot volume fractions and particle sizes. A new approach to optical pyrometry has been developed to measure temperatures where the other techniques fail due to the presence of soot. Our goal has been to obtain a more fundamental understanding of the important fluid dynamic and chemical interactions in these flames so that this information can be used effectively in combustion modeling.

DOE National Laboratories

An Expert Ab Initio Transition-State-Theory-Based Master Equation Code

Institution:	Argonne National Laboratory
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Principal Investigator:	Klippenstein, Stephen
Sr. Investigator(s):	
Students:	0 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$526,000

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) *ab initio* electronic structure explorations of the potential energy surface, (2) microcanonical TST calculations of the isomerization and dissociation rate constants implementing the *ab initio* calculated rovibrational properties, (3) a model for the rate of collision induced transitions in energy and angular momentum, and (4) the solution of the master equation representing the time dependence of the energy resolved species populations in terms of these microcanonical rate constants for dissociation, isomerization, and energy transfer. The latter solution yields temperature- and pressure-dependent phenomenological rate coefficients directly for use in chemical kinetic modeling. Current software implementations of the AITSTME approaches have various limitations that constrain their utility in several aspects. We propose to develop 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 would 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.

Chemical Dynamics in the Gas Phase

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Principal Investigator:	Pratt, Stephen
Sr. Investigator(s):	Davis, Michael, Argonne National Laboratory Klippenstein, Stephen, Argonne National Laboratory Harding, Lawrence, Argonne National Laboratory Macdonald, Glen, Argonne National Laboratory Michael, Joe, Argonne National Laboratory Shepard, Ron, Argonne National Laboratory Sivaramakrishnan, Raghu, Argonne National Laboratory Tranter, Robert, Argonne National Laboratory Ruscic, Branko, Argonne National Laboratory
Students:	4 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$4,475,000

PROGRAM SCOPE

The goal of this program is to develop a fundamental understanding of the elementary chemical reactions, non-reactive energy transfer processes, and coupled kinetics processes involved in combustion. The basic scientific approach is to combine 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. The group's staff members are split roughly 50/50 into theory (including modeling) and experiment. The theoretical effort embraces both large-scale 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 also being developed, along with approaches for global uncertainty quantification and sensitivity analyses. The experimental effort encompasses state-resolved measurements in flow tubes at low temperatures, thermal reaction kinetics measurements in shock tubes at high temperatures, and photoionization and photodissociation measurements of thresholds and state-resolved product distributions. Reaction rates, branching ratios (between different neutral products or between ionic and neutral products), product distributions, the effect of initial vibrational excitation on reactivity, and ion-cycles for thermochemical information are all being examined. Thus, both the theoretical and experimental components of the program are vertically integrated to span a wide range of phenomena relevant to the study of chemical reactivity. Furthermore, the group's greatest asset is the synergy that results from the strong interaction between the theoretical and experimental efforts. Taken as a whole, the group's work is designed to provide a fundamental understanding of both major and trace reactions of importance in combustion.

Argonne-Sandia Consortium on High-Pressure Combustion Chemistry

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Sr. Investigator(s):	Sivaramakrishnan, Raghu, Argonne National Laboratory Tranter, Robert, Argonne National Laboratory Georgievskii, Yuri, Argonne National Laboratory Harding, Lawrence, Argonne National Laboratory Miller, James, Argonne National Laboratory Davis, Michael, Argonne National Laboratory Michael, Joe, Argonne National Laboratory Ruscic, Branko, Argonne National Laboratory
Students:	3 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$925,000

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. Such accurate chemical models will aid in the effective use of novel alternative fuels, in the development of advanced engine designs, and in the reduction of pollutants. 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 through feedback loops at all levels of chemical complexity. We are currently developing and testing the methodology for propane and 1-butanol as key prototype fuels, and will extend this approach to a general fundamental theory of pressure effects. 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 and also interacts closely with the Princeton-led Combustion Energy Frontier Research Center.

Pressure Dependence of Combustion Reactions: Quantum Inelastic Dynamics on Automatically Generated Potential Energy Surfaces

Institution: Argonne National Laboratory
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Principal Investigator: Wagner, Albert
Sr. Investigator(s):
Students: 0 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding: $250,000

PROGRAM SCOPE

We will improve current methods for automatically generating potential energy surfaces and extend the application of these methods to inelastic processes involving chemically activated molecules colliding with buffer gases in a combustion environment. With these potential energy surfaces, we will carry out inelastic quantum dynamics for energy ranges up to the zero-point corrected threshold of elimination or isomerization of the chemically activated molecule. These quantum dynamics calculations will improve the predictive quality of pressure dependence calculations for elementary combustions reactions and will examine mechanistic issues as yet unresolved.

Gas-Phase Molecular Dynamics

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Sr. Investigator(s): Sears, Trevor, Brookhaven National Laboratory
Yu, HuaGen, Brookhaven National Laboratory
Students: 4 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding: $1,600,000

PROGRAM SCOPE

The Brookhaven Gas Phase Molecular Dynamics group develops and applies spectroscopic and theoretical tools to advance our understanding and predictive knowledge of the energetics, chemical reactivity, and kinetics of simple molecular systems of importance in combustion. We are particularly interested in understanding molecular collisions that lead to exchange of energy, angular momentum, or a change in the electronic states of the collision partners and how these collisions influence laser diagnostic measurements and reaction kinetics. New directions in spectroscopy include the use of time-resolved, sub-Doppler saturation methods and the development and application of frequency comb-based spectrometers to research problems in surface science and catalysis. Theoretical research is directed toward development and application of efficient and accurate computational methods for studying the spectroscopy, chemical reaction kinetics, and dynamics of small and medium-sized molecules. Current theoretical research thrusts are directed toward exploring the reactivity of radicals and reactions on multiple potential energy surfaces, and the ring-opening mechanisms of oxygen and nitrogen-containing heterocyclic hydrocarbons, as will be increasingly important in many biofuels. The knowledge and methods developed in this program are shared within the community of scientists and engineers devoted to improving the efficiencies and reducing the emissions of hydrocarbon combustion.

FY 2012 HIGHLIGHTS

We have implemented a dual-beam noise-reduction scheme well suited to commercial Fourier Transform Infrared spectroscopy with fiber-laser-based supercontinuum sources. The brightness and spatial coherence of the laser source facilitates multipass geometries, and simple numerical processing of dual-beam interferograms permits the measurement of weak absorption spectra with sensitivity close to the shot-noise limit, despite fluctuations in the supercontinuum intensity and spectrum.

A theoretical study of the pathways for oxidative ring-opening in morpholine, a six-membered ring with oxygen and nitrogen heteroatoms, was undertaken as a prototype for distinct combustion behavior in biofuels, many of which are more complex than fossil hydrocarbons. A distinctive low-energy path to ring opening has been identified following molecular oxygen addition to a carbon-centered morpholinyl radical: internal hydrogen abstraction from across the oxygen atom, followed by a low-barrier loss of OH accompanied by ring opening. The analogous reaction is inaccessible in cyclohexane oxidation and may be a previously neglected step in the low temperature combustion of morpholine and related fuels.

Research Associates: Goncharov, Vasily; McRaven, Chris; Forthomme, Damien; Dholabhai, Pratik

Chemical Dynamics Beamline Facility

Institution:	Lawrence Berkeley National Laboratory
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Sr. Investigator(s):	Ahmed, Musahid, Lawrence Berkeley National Laboratory Wilson, Kevin, Lawrence Berkeley National Laboratory
Students:	3 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$1,643,000

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 (1) determine the microscopic details of the mechanisms and dynamics of primary dissociation processes and elementary chemical reactions; (2) explore the properties and decay dynamics of molecules in highly excited, transient, or metastable states; (3) study the structure, energetics, and chemical reactivity of highly reactive polyatomic radicals, unusual transient species, droplets, aerosols, large biomolecules, and clusters; (4) develop new spectroscopic and dynamical tools such as imaging detection of photoelectrons, 2 color pump-probe spectroscopies, and pulsed field ionization techniques; (5) 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; and (6) 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 2012 HIGHLIGHTS

- Combustion Chemistry: from in situ flame sampling of reactive intermediates and nanoparticles to isomer-resolved product detection of elementary chemical reactions

- Heterogeneous, Atmospheric, and Environmental Chemistry of Particulate Matter
- Biomolecule Energetics
- Laser Ablation
- Low Temperature Chemistry of Planetary Atmospheres

Combustion Chemistry

Institution:	Lawrence Berkeley National Laboratory
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Principal Investigator:	Brown, Nancy
Sr. Investigator(s):	Frenklach, Michael, Lawrence Berkeley National Laboratory
Students:	0 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$260,000

PROGRAM SCOPE

Combustion processes are governed by complex interactions among chemical kinetics, energy transfer, transport, and fluid mechanics. Understanding these interactions offers the possibility of optimizing combustion processes. The objective of this research effort is to address fundamental issues of chemical reactivity, molecular transport, their use in combustion models, and how their uncertainties affect model fidelity. Our long-term research objective is to contribute to the development of reliable combustion models that can be used to understand and characterize the formation and destruction of combustion-generated pollutants. Brown and Frenklach emphasize studying chemistry and transport at both the microscopic and macroscopic levels. To contribute to the achievement of this goal, their current activities are concerned with five tasks: (1) develop models for representing combustion chemistry and transport at varying levels of complexity to use with reactive flow models to describe combustion processes, (2) develop and apply tools to facilitate building chemical mechanisms and to quantify their uncertainty, (3) model and analyze combustion in multi-dimensional flow fields, (4) determine new reaction pathways and their kinetics, and (5) build models for soot formation and destruction.

FY 2012 HIGHLIGHTS

We determined the most suitable potential and approach for computing thermal diffusion factors for binary mixtures by performing a detailed statistical analysis of over 100 experiments, 7 potential and 5 different approaches for determining the thermal diffusion factor.

Using sensitivity analysis, we determined that transport properties do not provide a constraint on the intermolecular potential, except possibly at very low temperatures.

Theoretic analysis of the thermodynamic and kinetic stability of graphene-edge oxiradicals revealed their dependence on the location of the radical site, which indicated that oxidation should predominantly remove armchair and corner-zigzag sites and leave resistant-to-oxidation inner zigzag sites essentially intact, thus anticipating proliferation of zigzag-edge surfaces on soot particles formed in combustion environments.

The thermodynamic and kinetic stability was explained by the degree of aromaticity developed in the molecular moieties.

Gas-Phase Chemical Physics

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Principal Investigator:	Neumark, Daniel M.
Sr. Investigator(s):	Head-Gordon, Martin, Lawrence Berkeley National Laboratory Lester, William A., Lawrence Berkeley National Laboratory Leone, Stephen R., Lawrence Berkeley National Laboratory Millier, William H., Lawrence Berkeley National Laboratory
Students:	5 Postdoctoral Fellow(s), 3 Graduate(s), 0 Undergraduate(s)
Funding:	$1,782,000

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 2012 HIGHLIGHTS

- Radical Photochemistry and Photophysics
- Molecular Reaction Dynamics for Combustion – Stephen R. Leone
- Development and Applications of Electronic Structure Theory
- Quantum Monte Carlo for Chemical Physics
- Theory of Atomic and Molecular Collision Processes

An Expert AB Initio Transition-State-Based Master Equation Code

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Sr. Investigator(s):	Zador, Judit, Sandia National Laboratories-Livermore
Students:	1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$240,000

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 will develop 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.

Chemical Composition of Soot Nanoparticles

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Sr. Investigator(s):	Hansen, Nils, Sandia National Laboratories-Livermore
Students:	1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$144,000

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.

Combustion Research Facility

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Students:	12 Postdoctoral Fellow(s), 0 Graduate(s), 3 Undergraduate(s)
Funding:	$10,650,000

PROGRAM SCOPE

This work proposal covers in-house 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 chemistry and combustion diagnostics. In experimental studies, an emphasis is maintained on the development and application of advanced, laser-based detection technologies. In chemistry, specific projects include studies in 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 of combustion research 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 the CRF in three ways. First, it supports critical in-house 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 external combustion scientists to the CRF to participate in ongoing research and to share in technological advances.

High Pressure Combustion Chemistry: From Fundamentals to Accurate Models

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Students:	2 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$815,000

PROGRAM SCOPE

The goal of this project is to develop accurate models for combustion chemistry based on a detailed understanding of the fundamental effects of high pressure on combustion kinetics. The project addresses two principal scientific challenges. (1) Current combustion chemistry models have been developed and validated by using low-pressure experiments, and they fail at the high pressures of real devices. (2) Accurate chemical models are required for the effective use of novel alternative fuels, for the development of advanced engine designs, and for the reduction of pollutants.

This project addresses these scientific challenges through (1) an emphasis on implementing the integrated modeling, experiment, and theory paradigm through feedback loops at all levels of chemical complexity; (2) the design and implementation of novel experiments, theory and modeling to probe high-pressure combustion kinetics from elementary reactions, to sub mechanisms, to flames; (3) the development of a test methodology for a few key prototype fuels (propane, N-heptane, and 1-butanol) that will be extended to a general fundamental theory of pressure effects; and (4) the expansion and enhancement of existing collaborations between Argonne and the Combustion Research Facility at Sandia National Laboratories, through this new thrust in high-pressure combustion chemistry.

Geosciences

Institutions Receiving Grants

Molecular Basis for Microbial Adhesion and Geochemical Surface Reactions: A Study Across Scales

Institution:	Alabama, University of
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Principal Investigator:	Dixon, David
Sr. Investigator(s):	
Students:	0 Postdoctoral Fellow(s), 1 Graduate(s), 1 Undergraduate(s)
Funding:	\$0 (Research was supported with prior fiscal year funding.)

PROGRAM SCOPE

The current work is a computational chemistry effort focused on the molecular level description of the interactions of Gram-negative microbial membranes with materials in the subsurface. An improved understanding of the molecular processes involved in microbial metal binding, microbial attachment to mineral surfaces, and, eventually, oxidation/reduction reactions (electron transfer) that can occur at these surfaces and are mediated by the bacterial exterior surface is being developed. The project is focused on the interaction of the outer microbial membrane, which is dominated by an exterior lipopolysaccharide (LPS) portion, with the mineral goethite and with solvated ions, for example uranyl and metal dications. The approach uses modern computational electronic structure methods and has three components: solvation energies and structures of ions in solution, prediction of the acidity of the critical groups in the sugars in the LPS, and binding of metal ions to representative models of the sugar anions and to phosphate groups. The interactions of the sugars with metal ions are expected to dominate much of the microscopic structure and transport phenomena in the LPS. An important aspect of the structure of the LPS membrane as well as ion transport in the LPS is the ability of the sugar side groups such as the carboxylic acids and the phosphates to bind positively charged ions. The acidity of the acidic side groups is studied to understand the ability of these groups to bind metal ions. The acidities of the metal ions in solution provide information about the size of the first solvation shell. The binding of the cations in media with different dielectric constants and the binding of uranyl to differently charges phosphate groups with the presence of varying amounts of water is being studied.

FY 2012 HIGHLIGHTS

Anhydrous and hydrated complexes of UO_2^{2+} with the phosphate anions $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}; the microsolvated $H_xPO_4^{3-x}(H_2O)_4$, x = 0-3 complexes; and water ligands were studied at the density functional theory level as isolated species and by self-consistent reaction field calculations with the COSMO parameters. Major binding modes, geometries, and vibrational frequencies for these complexes are compared to experiment where possible. The thermodynamics of binding, the equilibrium constants for the reactions of UO_2^{2+} with phosphate and water ligands, and displacement reactions were studied; and good agreement with the available experimental data was found. The acidities of UO_2^{2+}/phosphate/H_2O complexes have been predicted and examined in terms of the structure about the uranyl. The acidities of other metal ions in water were calculated and used to determine the size of the first solvation shell. The +2 cations require only the first solvation shell; but more positive cations require more solvation shells to match the experimental acidities, showing that the positive charge delocalizes past the first shell.

Computational and Experimental Investigations of the Molecular Scale Structure and Dynamics of Geologically Important Fluids and Mineral-Fluid Interface

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Principal Investigator:	Bowers, Geoffrey
Sr. Investigator(s):	
Students:	0 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$76,000

PROGRAM SCOPE

The main objective of this joint research effort with Prof. R. James Kirkpatrick of Michigan State University is to improve our molecular-scale understanding of the structure, dynamics, and reactivity of geochemically important fluids, fluid-mineral interfaces, and confined fluids using computational modeling and experimental methods sensitive to molecular-scale behavior, principally nuclear magnetic resonance spectroscopy. Molecular scale knowledge of the structure and dynamics of aqueous fluids, how these fluids are affected by mineral surfaces and molecular-scale nano-confinement, and how water molecules and dissolved species interact with mineral surfaces is essential to understanding the fundamental chemistry of a wide range of geochemical processes relevant to energy geoscience (e.g., contaminant storage and environmental transport) and is one of the most important cross-cutting fundamental research issues in effectively addressing the Grand Challenges in basic energy sciences. The specific Alfred University project objectives are to perform a comprehensive molecular scale investigation of the structure and dynamics of amorphous calcium carbonate/magnesium carbonate (ACMC) formation and to investigate the structure, dynamics, and energetics of ions and $^{2}H_2O$ at clay-water interfaces using nuclear magnetic resonance (NMR) spectroscopy.

FY 2012 HIGHLIGHTS

We have made significant progress in meeting each of these objectives. Our study of alkali metal and H_2O dynamics in alkali metal-smectites was completed, revealing a new mechanism for $^{2}H_2O$ motion within 5Å of a smectite surface. This work was featured on the December 1 cover of the Journal of Physical Chemistry C. We completed similar studies of Ca-hectorite during the current fiscal year and observe the same type of dynamic behaving for $^{2}H_2O$. Recently obtained relaxation data support the idea of GHz-scale librational motion along the H_2O C_2 symmetry axis. Novel ^{43}Ca NMR studies of Ca^{2+} in Ca-hectorite revealed that Ca^{2+} adheres to our recently reported general principle for alkali metal smectites that as ionic radius decreases and hydration energy increases, ion motion becomes dominated by isotropic 2D or 3D diffusion at lower temperature. Manuscripts detailing this work and related computational molecular modeling studies are currently in the final stages of preparation. Our group also broke new ground by performing systematic ^{43}Ca and ^{25}Mg NMR studies of ^{43}Ca-enriched ACMCs and related hydrated carbonates, the results of which lead to several manuscripts in preparation and one paper published in Chemistry of Materials. Research results obtained during this past grant year also supported a successful peer-reviewed renewal of our science-theme proposal for high-field NMR, electron microscopy, and micro-XRD instrument time at Pacific Northwest National Laboratory for the remainder of the current grant and beyond.

Physical Mechanisms Controlling CO2-Brine Capillary Trapping in the Subsurface

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Funding:	$122,000

PROGRAM SCOPE

Capillary trapping is a somewhat under-explored mechanism in geologic sequestration of CO_2. Central to capillary trapping is its pore-scale nature: pore-scale geometry, fluid velocities, as well as brine- CO_2 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 CO_2 into the brine, and allowing gaseous CO_2 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 CO_2. 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 2012 HIGHLIGHTS

We built a flexible lattice Boltzmann simulator that implements van der Waals type equations of state. This code is fast (GPU and parallel processing capable), supports a range of computer hardware, and can be extended beyond the immediate objectives of the current project. The code will be open-sourced in about a year. We found that the range of temperature and pressures for relevant reservoir conditions can easily be simulated. Although the simulated EOS are qualitatively consistent with experimental data, we also found that modifications to the parametrization of the LBM EOS are necessary to obtain a better quantitative match for the water-vapor and water/brine- s.c. CO_2 systems. Currently, we are refining the EOS implementation to obtain a better match with experimental EOS data for the pure CO_2 system and are implementing an interaction term between water/brine and s.c. CO_2. We will also implement mixed wettability into the model, allowing water-wet and oil-wet pores to co-exist within the simulated domain. This will likely lead to a moderate loss in computational speed and somewhat higher memory requirements.

Collaborative Research: Analysis and Interpretation of Multi-Scale Phenomena in Crustal Deformation Processes

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Funding:	$175,000

PROGRAM SCOPE

The goal of this project is to bring the techniques of modern statistical physics to bear on understanding multi-scale phenomena in crustal deformation processes. This year, we have extended our analysis to the effect of damage on processes such as earthquakes and fracturing in materials. To understand these processes, we have concentrated on three areas: (1) the effect of fault damage on Gutenburgh-Richter (GR) scaling in earthquake fault systems, (2) the effect of fault damange on the nature and location of phase transitions such as critical points and spinodals, and (3) the effect of fault damange on the fracture process or nucleation in general. We use simulations in simplified models as well as statistical field theories. An important aspect of our work is that we concentrate on systems with long-range interactions since the physics of the crust is determined by long-range elastic forces and the physics of long-range forces is different from the more intensely studied short-range systems.

FY 2012 HIGHLIGHTS

(1) We have shown that GR scaling is explained by including damage. Models of faults with no damage show GR scaling over an extensive range. The scaling is controlled by a spinodal critical point (SCP). As damage is added to the model, the range of GR scaling shrinks. This is also seen in actual fault data. However, the physics is still controlled by a SCP as evidenced by data collapse of the scaling plots. If the number of events with moment m is added up over models with different amounts of damage, a GR scaling emerges with a different scaling exponent than individual faults but also with a larger range. The scaling exponent can vary over a small range depending on the statistical weight given to individual faults in the sum. This is seen in real fault systems in which scaling exponents vary as one goes from one fault system to another.

(2) The spinodal critical point that is responsible for GR scaling is smeared by the presence of damage. This is the reason that the GR scaling range shrinks. This also results in a change of the nature of fracture and nucleation as damage is added. In addition, we can sharpen the spinodal by making the range longer so that in mean-field systems with an infinite range, the spinodal is not smeared. This makes the analysis of the effect of damage on the spinodal somewhat subtle. This is also important since fracture is controlled by the spinodal in the crust due to the long-range elastic force.

(3) In our models, damage acts as a nucleation site. This is somewhat surprising in the case of vacancies where the critical droplet actually appears preferentially in the region of the empty sites.

Multiscale Framework for Predicting the Coupling Between Deformation and Fluid Diffusion in Porous Rocks

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Funding:	$125,000

PROGRAM SCOPE

The objective of this program is to develop a predictive multiscale framework to hierarchically homogenize the constitutive behavior of fluid-saturated rocks, directly linking the continuum representation with granular processes, in areas of severe deformation, such as deformation banding, where phenomenology breaks down.

In this project, a predictive multiscale framework will be developed to simulate the strong coupling between solid deformations and fluid diffusion in porous rocks. We intend to improve macroscale modeling by incorporating fundamental physical modeling at the microscale in a computationally efficient way. This is an essential step toward further developments in multiphysics modeling, linking hydraulic, thermal, chemical, and geomechanical processes. This research will focus on areas where severe deformations are observed, such as deformation bands, where classical phenomenology breaks down.

At Caltech, we will concentrate on the computational and experimental aspects of this project.

FY 2012 HIGHLIGHTS

We obtained samples of Aztec sandstone from the Valley of Fire (Nevada). Specimens were scanned at the synchrotron APS, at Argonne National Laboratory to obtain x-ray CT images. Using these images, we are able to non-destructively reconstruct the three-dimensional microstructure of sandstones inside compaction bands for the first time. We do this using new computational techniques that use level set methods and concepts from graph theory. We obtain not only porosity but also other important microstructural attributes, such as occluded/connected porosity and geometrical tortuosity.

The framework uses a hybrid lattice Boltzmann/finite element scheme to obtain homogenized effective permeability at specimen-scale. Results obtained from the Aztec sandstone samples reveal approximately an order of magnitude permeability reduction within the compaction band. This is less than the several orders of magnitude reduction measured from hydraulic experiments on compaction bands formed in laboratory experiments and about one order of magnitude less than inferences from two-dimensional images of Aztec sandstone. Geometrical analysis concludes that the elimination of connected pore space and increased tortuosities due to the porosity decrease are the major factors contributing to the permeability reduction. In addition, the multiscale flow simulations also indicate that permeability is essentially isotropic inside and outside the compaction band.

Anisotropy and Residual Stresses in Sedimentary Rocks: A Synchrotron and Neutron Diffraction Study

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PROGRAM SCOPE

The direction-dependent microstructural properties of shales are of critical importance for hydrocarbon exploration, hydrocarbon reservoirs, storage sites for nuclear waste, as well as CO_2 repositories. The microstructure of these very fine-grained rocks, composed of many minerals and, particularly, clays, is complex and poorly known. By using novel techniques, such as high energy synchrotron diffraction and X-ray microtomography (XMT), combined with transmission electron microscopy (TEM), it has become possible to quantify microstructural features and use those observations as a basis for models to predict macroscopic properties such as acoustic velocities. Thus fundamental research in mineralogy and crystallography, on the elementary scale, provides crucial information for oil and gas recovery.

FY 2012 HIGHLIGHTS

Shales are sedimentary rocks composed of minerals such as quartz, feldspars, and phyllosilicates. The latter have a sheet structure and platelet morphology. During sedimentation and compaction, they become aligned and form a regular pattern of preferred orientation. They are extremely fine-grained, and only TEM can reveal individual grains and their morphology. The bulk alignment pattern of platelets cannot be measured grain-by-grain but is captured by x-ray diffraction. Synchrotron diffraction images can then be deconvoluted to quantify the pattern of preferred orientation. But crystals alone are only one ingredient responsible for anisotropy of shales. Another contribution is porosity, which can now be measured by three-dimensional synchrotron x-ray microtomography. Combining this information on crystallite alignment, crystallite shape, and pore structure through sophisticated averaging methods, we can now predict macroscopic anisotropic properties based on measured microscopic features. With a new self-consistent model, we were able to calculate anisotropic elastic properties of Kimmeridge shale, well within error limits, and we plan to apply the method to other samples.

There has been great interest for this work from colleagues across the world, and our research team continues to contribute new information on shales of different origin, ranging from North Sea, Nigeria, Texas, Australia, Switzerland, Saudi Arabia, and Germany. Also, to make the new methods available for a wider circle, we are organizing this fall a workshop at LBL and have attracted a large group of participants. Results obtained in 2012 have been reported in seven journal publications.

Adding Reactivity to Structure: Oxygen-Isotope Exchanges at Structural Sites in Nanometer-Size Aqueous Clusters

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Funding:	$154,000

PROGRAM SCOPE

Trends for geochemically important reactions can be organized by examining molecular model compounds in experiments that couple well to simulation. Reactions that lend themselves well to this analysis include isotope-exchange reactions; we probe these reactions at the molecular scale, in both experiment and simulatin, in order to establish reliable methods for predicting rates that cannot be experimentally studied. Much research in the last period emphasized materials that are both geochemically interesting and have applications at water-splitting catalysts for energy production.

FY 2012 HIGHLIGHTS

(1) Casey and Rustad published a model in *Nature Materials* for the dissolution of oxides that links observations at many scales. They identified low-energy metastable configurations that form from the breaking of weak bonds between metals and underlying highly coordinated oxygen atoms, followed by facile hydroxide/hydronium/water addition. The mediation of oxygen exchange by these stuffed structures suggests a new view of the relationship between structure and reactivity at the oxide-solution interface. This paper attracted much attention and was discussed in an associated News and Views commentary by Paul Fenter.

(2) Greg McAlpin was funded by this project and received the Best Dissertation Award, 2012 in the Department of Chemistry. His work examined materials from the “artificial leaf” of Nocera and others, which is able to harvest up to 4.7% of incident photonic energy for water-splitting and solar fuel production. It is made of earth-abundant elements and mimics the structure and functionality of materials precipitating in the Hanford Site and the Mn oxygen-evolving complex in photosystem II. At its heart is a clay-like material that catalyses the difficult oxygen half of the water-splitting reaction. McAlpin used electron-paramagnetic resonance (EPR) to characterize the resting state of the film’s prepared in phosphate buffers and showed that the formation of a Co(IV) species was closely associated with water oxidation activity. This work was expanded to include extensive study of this system prepared in a variety of buffers and polarizing potentials, allowing us, with collaborators both at UCD and other institutions, to develop a thermodynamic model for the structure and mechanism of this water oxidation. We believe it to be a layered cobalt-hydroxide material with interlayer buffer ions acting as proton shuttles, much like material found in contaminated soils.

These findings, collected in collaboration with other researchers from UCD, U. Wisconsin, and MIT, led us to delve further into the characterization of Co-oxo and Co-peroxo containing species as models for the structure and reaction pathway for this system. CW and Pulse EPR in conjunction with DFT studies were used to investigate the electronic structure of a Co(IV)Co(III)3 cubane model complex and found that the unpaired formally Co(IV) electron was delocalized over the entire core of structure. McAlpin is now building models for the proposed peroxo intermediate.

Statistical Mechanics of Defect-Mediated Dynamics in Complex Geomaterials

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Funding:	$175,000

PROGRAM SCOPE

Complex geomaterials are rocks and minerals representing a subset of complex systems, which are typically defined to be high-dimensional (many degrees of freedom) systems having interacting components that are subject to a nonlinear evolution law. In such systems, one finds a variety of cooperative phenomena that are typically not a property of the structure of the system, but instead emerge from the dynamics (emergent phenomena). These cooperative phenomena lead to coherent structures or space-time patterns. Rock deformation processes, which include plasticity, fracture, and grain boundary dynamics, are examples of this category of phenomena. Fields of dislocations, defects, microcracks, mis-matching grain boundaries, shear and tensile fractures, and other structures of material disorder are ubiquitous. These objects can be called the “defect field” or the “disorder field”. For small amplitude deformations (strains), the material can be considered linear elastic, but for larger strains, elements of the disorder field become mobile, and may migrate, diffuse, or grow in amplitude under application of stress. For high enough stress, the material begins to exhibit plastic deformation. As stress continues to increase, the limit of stability is eventually attained and the material fails.

FY 2012 HIGHLIGHTS

In this year’s research program, we used data, theory, and numerical simulations to develop an understanding of the basic processes of rock damage and deformation. In a new study of sliding friction, we used a model in which a major sliding event induces a weakening of the failure threshold. We find that the amount of weakening is a scaling field similar to the pressure P in a thermal phase transition, or the external H-field in magnetic phase transition. Under certain conditions, we also find that the scaling exponents for the clusters of slipped asperities are the same, within error, to the values for mean field percolation.

We also focused on tensile fracture, extending a model that was first proposed by us in 1989. Here we find that, depending on the physics of the cohesion or pinning force, a variety of symmetry-breaking transitions can be identified and understood. Several of these transitions were seen previously in studies of Ising models. Finally, we also apply a coarse-grained version of the model to the fracking problem. We find that growth of the frack is similar to the problem of surface growth using either particle deposition or percolation cluster growth, as obtained from the Leath algorithm. We find that the scaling exponent of the correlation function for the surface growth tensile field is similar to values obtained from particle deposition on a surface as described by the Karder-Parisi-Zhang equation.

Thermodynamics of Minerals Stable Near the Earth's Surface

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Funding: $254,000

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 H_2O. 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 2012 HIGHLIGHTS

The first thermodynamic study of this structure measured enthalpies of solution for two salts of the ε-Al13 Keggin and derived heats of formation for these two isomorphous species. Both of these salts exhibited a formation from oxides that was exothermic, with a decomposition to gibbsite that was also exothermic. This provided experimental evidence to support that these clusters are metastable intermediates. Additionally, an exchange reaction between sulfur and selenium in 5N HCl displayed the relative affinity for the ε-Al13 Keggin for selenate in the solid form and sulfate in 5N aqueous hydrochloric acid. This study produced the methodology upon which we continue to measure these aluminum cluster compounds.

Stable Isotope Probe of Nano-Scale Mineral-Fluid Redox Interactions

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Funding:	$162,000

PROGRAM SCOPE

Our goal is to study how stable isotopes fractionate at an aqueous/solid interface during electrochemical reduction 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. 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 an electrochemically-controlled process at the electrode interface, 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. Our results imply that isotope behavior at a heterogeneous interface is sensitive to the kinetic behavior of the interface. Based on these and other experiments and theory showing and predicting significant and rate-dependent fractionations of isotopes at reacting interfaces, we are developing a new theory of interface reactivity which explains and predicts this behavior.

FY 2012 HIGHLIGHTS

Thus far, we have measured similar isotope electrodeposition behavior in Fe, Zn, Li, Mo, and Cu. This past year, we have succeeded in separating out the influence of mass transport from the much larger redox-influenced fractionation at the electrode. In addition, we performed a series of measurements of iron isotope fractionation in a silicate melt sample exposed to redox field. The results showed a ~1ppt isotope fractionation across a ~1V redox gradient. Finally, we have developed a theory of mass-dependent isotope behavior at phase boundaries at equilibrium that predicts kinetic isotope fractionations close to equilibrium, given information about the equilibrium isotope fractionation, and three boundary parameters that are not dependent on isotopes. In the next period, we will test the predictions of this new theory against existing data. As a test of our theory, we plan to perform experiments in which isotope fractionation is measured during both oxidation processes and reduction processes as a function of temperature.

Development and Application of Next Generation Parameter Free Petascale Simulation Technology for Solution Species, Nanoparticles, and Geochemical Interfaces Under Extreme Conditions

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Funding:	$159,000

PROGRAM SCOPE

First principles simulations methods are being developed and applied to the study of the chemical behavior of metal ions, their counter ions, and oxo-hydroxo hydrolytic polyions in aqueous solutions. The understanding of the aqueous chemistry of these species is essential to the interpretation of processes such as the formation of minerals, the sequestration of CO_2, the storage of nuclear waste, and the transport of toxic materials. The simulation methods that are being used and developed allow parameter-free prediction of properties over the wide range of conditions encountered in geological applications and will utilize the rapidly expanding power of leadership class computers. This year, a natural extension of the program to include first principles calculations of the electronic structure and chemical properties of the transition metal (primarily Fe) oxide/solution interfaces has been initiated.

FY 2012 HIGHLIGHTS

First principles dynamical simulations and electron scattering calculations have been shown to provide near quantitative agreement with new and existing XAFS measurements for a series of transition metal ions interacting with their hydration shells via complex mechanisms. This analysis does not require the development of empirical interparticle interaction potentials nor does it require structural models of hydration. However, it provides consistent parameter-free analysis and improved agreement with the first and second shell structure, symmetry, dynamic disorder, and multiple scattering. DFT+GGA MD methods provide high agreement and efficient simulation. However, improvements are observed when exact exchange is included. Improvement of the pseudopotential description of the atomic potential was necessary for very detailed agreement. The first principles nature of this analysis approach supports application to complex systems.

Two new programs have been initiated this year. Methods of calculating the electronic structure of iron oxide solids (hematite and goethite) commonly encountered in natural environments are being applied and developed. Preliminary results show very good agreement between density functional theory results and observations for water saturated goethite 001 surfaces in the subsurface region. However, there appears to be large differences between the interpretation of the data and calculations at the interface. Calculations can be done at the DFT+U, DFT+GGA, and DFT+GGA+exact exchange levels. These results will be finalized in the continuing program, and agreement will be reconciled with observations. In addition, new parallels in time simulation algorithms have been developed and applied to first principles molecular dynamics simulations of realistic complexity. We have shown a significant parallel speed up, thus providing a means to explore longer time domains via distributed (cloud) computing. These new approaches support the application of a simulation method to higher level electronic structure calculations (e.g., MP2, CCSD) necessary for many complex geochemical environments.

Fault-Related CO_2 Degassing, Geothermics, & Fluid Flow in Southern California Basins—Physiochemical Evidence & Modeling

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Funding:	$97,000

PROGRAM SCOPE

This collaborative study attempts to quantify fluid flow, subsurface methane migration, and diagenetic effects within deforming faults in a seismically active transpressional setting. The emphasis is on active faults and young (Tertiary strata) petroleum fields in southern California. Faults include the Refugio fault in the Transverse Ranges, the South Ellwood fault in the Santa Barbara Channel, and the Newport-Inglewood fault 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 fault properties and history, including geochemical signatures in carbonate that characterize rapid CO_2 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 2012 HIGHLIGHTS

Permeability of the South Ellwood fault, which bounds the north edge of the offshore south Ellwood oil field, is being estimated by several methods, including changes in isotopic and elemental formation water composition over a four-year time period resulting from sea water being drawn down the fault zone into the reservoir; changes in gas seep rate to the sea floor during producing versus idle well production; and the attenuation and lag in a two-week tidal signal record measured within the reservoir that is one kilometer below the sea bed in close proximity to the South Ellwood fault.

In the LA basin, isotopic and elemental fluid composition is being used to characterize fluid composition as a function of temperature and diagenetic processes. Helium isotopes are also being measured as an indicator of gas migration in the basin. At temperatures greater than 100°C, waters have low Sr isotopic ratios due to alteration of feldspar and volcanics, whereas samples at lower temperatures (shallow depth) have radiogenic values. We are currently evaluating sidewall cores from a newly drilled deep well that crosses the N-I fault zone to establish fault zone diagenetic processes.

Rapidly precipitated carbonate (well scales, flowstone in tunnels) have oxygen isotopic values that are more negative than predicted from equilibrium. A collaborative study with Professor Sidney Omelon, University of Toronto, focusses on the effects of crystallization rates on carbonate oxygen isotopic composition using degassing and mixing experiments. Results indicate that the rapid crystallization processes result in calcium carbonate with up to 25 per mil lighter oxygen than expected for "equilibrium." The work is relevant to sequestration and leakage of CO_2 gas from reservoirs.

GeoSoilEnviroCARS: A National Resource for Earth, Planetary, Soil and Environmental Science Research at the Advanced Photon Source

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Funding:	$882,000

PROGRAM SCOPE

GeoSoilEnviroCARS (GSECARS), a national synchrotron radiation user facility for earth science research at the Advanced Photon Source (APS, Argonne National Laboratory), consisting of an undulator beamline and a bending magnet beamline, is operated by the Center for Advanced Radiation Sources at the University of Chicago. GSECARS is jointly supported by NSF-EAR-IF. Synchrotron-based analytical techniques available at GSECARS include (1) x-ray fluorescence microanalysis, (2) x-ray absorption spectroscopy, (3) computed microtomography, (4) inelastic x-ray scattering, (5) x-ray diffraction and spectroscopy in the diamond-anvil cell with double-sided laser heating, (6) Brillouin spectroscopy coupled with x-ray diffraction, (7) x-ray diffraction and imaging in the large-volume press, and (8) powder, surface, and single-crystal diffraction.

Principal research areas include (1) speciation and microdistribution of metals and radionuclides in soils; (2) redox reactions, transport processes, and reaction kinetics of metals in soils; (3) carbon sequestration relevant processes; (4) sorption processes and reactions at mineral-water interfaces; (5) role of biota in transport processes; (6) oxidation states of igneous systems; (7) metal partitioning and speciation in hydrothermal fluids; (8) fluid transport dynamics in the subsurface; (9) equations-of-state of mantle phases; (10) rheology studies at high pressure; (11) determination of melting points and the densities and viscosities of melts at high pressure; and (12) phase relationships in mantle minerals and candidate core materials.

FY 2012 HIGHLIGHTS

GSECARS research was conducted by 352 unique scientists and students in FY 2012, and 100 papers were published in scientific journals. Examples of results include (1) observations of U(VI) sorption complexes and U(IV) nanoprecipitates on the magnetite (111) surface extend the range of conditions under which U(VI)–CO_3–Ca complexes inhibit U reduction; (2) geothermal waste fluids released in surface waters contained predominantly As(III) and create a localized area of arsenic contamination; (3) mercury was found to be bound to corrosion products, oxygen complexes, or sulfur in a variety of reactive materials proposed for groundwater treatment; (4) titanium substitutes for Si in zircon indicating that the Ti content of zircon at a given pressure is not only a function of temperature, but increases with decreasing silica activity; (5) gram-positive facultative anaerobe, *Cellulomonas* sp. strain ES6, removed U(VI) from solution simultaneously through precipitation with phosphate ligands and microbial reduction; and (6) silver-coated microspheres were useful for differentiating between biomass and fluid-filled pore spaces in computed microtomography (CT) images of porous media.

Kinetic Isotope Fractionation by Diffusion in Liquids

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Funding: $200,000

PROGRAM SCOPE

The overall objective of our research effort is to document and quantify kinetic isotope fractionations during chemical and thermal (i.e., Soret) diffusion in liquids (silicate melts and water) in both laboratory experiments and in natural settings. Isothermal diffusion couples are used to measure major element isotopic fractionation by chemical diffusion in natural composition melts using starting materials made from Mid-Ocean Ridge Basalt juxtaposed with a natural rhyolite glass or from rock powders from a coeval felsic and silicic magmatic systems in coastal Maine. The field component of our work involves finding natural analogues of isotopic fractionations seen in the laboratory and interpreting these in terms of dominant chemical transport mechanism (molecular diffusion versus magma mixing) in the natural system. A separate set of laboratory experiments involves quantifying thermal isotope fractionations that arise when a temperature gradient is maintained across an initially homogeneous fluid for a sufficient length of time. Both silicate liquids and water with dissolved salts are used for these thermal fractionation experiments. Numerical models reproducing the elemental and isotopic fractionation in water and in silicate systems are being developed and continuously refined in light of new experimental data.

FY 2012 HIGHLIGHTS

We have continued our laboratory experiments to document and calibrate isotopic fractionation by chemical and thermal diffusion in silicate liquids. The latest development involves our having found that the degree of isotopic fractionation in a multi-component system is not only a function of the concentration difference of the parent element in the diffusion couple but that it also depends on the direction in composition space. For example, for a given change in calcium concentration between the two end-members, we find different degrees of Ca isotopic fractionation when calcium counter-diffuses with a slow diffuser such as silicon (other elements being uniform) compared to a much larger isotopic fractionation when it counter-diffuses with a fast diffuser such as sodium. We have also continued field studies to sample contacts where melts of different compositions were juxtaposed. We now have a collection of more than thirty such samples from six separate localities in Maine. We have measured the concentration gradients in half these samples, and they are well suited for us to proceed with isotopic measurements.

As we begin to focus more on natural occurrences of isotopic fractionation by diffusion, we have had to confront the issue of fractionations due to diffusion from the melt into mineral grains. We recently completed a series of laboratory experiments on isotopic fractionation of lithium, iron, and magnesium into both olivine and pyroxene grains. One surprising result is that silicate minerals fractionate isotopes more effectively than silicate melts. Another surprise is that the diffusion profiles in minerals with a high concentration source at their surface often do not show a simple decreasing concentration in from the boundary, but rather the diffusant penetrates as a propagating step. We have developed a diffusion model that can explain this propagating step behavior and the associated isotopic fractionation based on the diffusant occupying different sites in the crystal lattice. We are still trying to understand the conditions that cause the diffusion profiles to be step-like in some cases and the more usual error function-like behavior in other cases. We are fairly certain that it must involve the concentration of vacancies, but we are still working on a more quantitative explanation.

Synchrotron X-Ray Microprobe and Microspectroscopy Research In Low Temperature Geochemistry

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Funding:	$226,000

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 µm (FWHM) are achieved resulting in a gain in flux/μm^2 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 2012 HIGHLIGHTS

Published research produced the following results. (1) Decreasing $Fe^{3+}/\Sigma Fe$ ratios in subduction zone basalts correlated with decreasing S concentrations suggesting that electronic exchanges associated with SO_2 degassing may dominate $Fe^{3+}/\Sigma Fe$ variations in the melt during differentiation. (2) Mine tailiing hardpan cements were found to include amorphous Fe arsenate and Fe oxyhydroxide with nearly all hardpan associated with historical arsenopyrite-bearing concentrate which provides a source of acidity, As^{5+}, and Fe^{3+} for secondary mineral precipitation. (3) Methylated forms of arsenic in contaminated soils were mainly associated with Fe-oxyhydroxides as sorption complexes. (4) Uraninite and coffinite are the principal U-rich minerals in the core material of a U-rich well in S. Carolina, consistent with the hypothesis that dissolution of partially oxidized Ca-rich uraninite occurring in the surficial biotite granite (or secondary coffinite in fracture zones) is likely the main source for the current high levels of U in nearby area wells. (5) An investigation of plant uptake and the potential for trophic transfer of nanoscale Au nanoparticles using model organisms demonstrated trophic transfer and biomagnification of gold nanoparticles from a primary producer to a primary consumer with important implications for risks associated with nanotechnology, including the potential for human exposure.

Non-Darcian Flow, Imaging, and Coupled Constitutive Behavior of Heterogeneous Deforming Porous Media

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Funding:	$99,000

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 oil and gas production/exploration and carbon sequestration. This project consists of theoretical and experimental work aimed at improving constitutive descriptions of the elastic-plastic deformation of porous geomaterials, particularly sandstone. The plastic response of geomaterials has been modeled using classical plasticity (originally developed for metals), adapted for geomaterials by use of non-associated flow (non-normality). The yield surface in stress space separates elastic from plastic response; in geomaterials, the plastic strain increment is not perpendicular to the yield surface. Thus, a plastic potential is used; this is the surface to which the plastic strain increment is perpendicular. However, the use of a plastic potential has recently been questioned, in part, because it admits the possibility of negative work. One of the primary goals of this project is to use a thermomechanics approach to derive elastic-plastic constitutive relations which are (1) representative of porous sandstone behavior and (2) thermodynamically sound. Such constitutive relations will be enormously useful for theoretical failure modeling and in large-scale computational simulations.

FY 2012 HIGHLIGHTS

(1) Project personnel were selected. Melissa Richards (PhD student) is conducting the theoretical work under Dr. Issen at Clarkson. Mathew Ingraham (senior member of technical staff, Sandia Labs) is conducting the experimental work. The project start was delayed because Richards was under contract to teach at Clarkson through May of 2012 and Ingraham completed his PhD in May 2012.

(2) Richards and Ingraham completed training on the fundamentals of the Collins and Houlsby (1997) approach to developing constitutive relations. Richards completed in-depth training on (a) the C&H thermomechanics approach and (b) traditional derivation methods for elastic-plastic constitutive relations.

(3) We completed strain partitioning of two Castlegate sandstone data sets from prior grants; and plotted yield surfaces in true stress space. We identified how to develop expressions for the Gibbs Free Energy (GFE). Initial expressions for two of the three GFE terms are taken directly from the Castlegate data. We are now investigating mapping methods to determine the third term, which distorts the elliptical yield surface in dissipative stress space to the well-known egg-shaped yield surface in true stress space.

Understanding the Grain-Level Properties of Rocks from Sub-Millimeter-Resolution Mechanical and Electromagnetic Measurements

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Funding:	$82,000

PROGRAM SCOPE

Material characterization of rock-fluid systems requires an array of measurement techniques and measurement length scales from the kilometer down to the atomic. To try to make a coherent and consistent picture of such complexity is well beyond our understanding at this time. However, the more modest goal of understanding the grain scale statics and dynamics of granular media and the sedimentation of shales and similar rocks is within our reach, both experimentally and theoretically. Further, at this length scale, there is a real opportunity to study up-scaling from grain scale properties to bulk measurements on rock cores.

FY 2012 HIGHLIGHTS

We have developed ultrasonic and electromagnetic scanning techniques that allow us to produce co-located maps of electrical and mechanical rock properties at the 100 micron scale or below. The purpose of this proposal is to exploit this new technology to develop a comprehensive picture of the interrelation of these fundamental properties and thereby reduce the ambiguity in geophysical, geological, and climatological interpretation. We have assembled a unique multi-disciplinary team to perform this work. We believe this work will have impact not only on the development of new energy sources but on broader environmental issues associated with these sources. In addition, we believe that detailed organic characterization of sediments at such fine scale could have implications for studies of global climate change.

We are currently doing measurements with students in Prof. Prasad's group on rocks of key importance. Also, we have begun to work with the USGS in Denver to apply our analytic techniques to an ongoing project of theirs on thermal maturation in oil shales.

Defining Fe and H Speciation during Olivine Carbonation Under Highly Reducing Conditions

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Funding:	$150,000

PROGRAM SCOPE

The water-rock reaction pathways that occur during the low-temperature (e.g., 25-150^{o}C) anoxic alteration of mafic and ultramafic rocks are not currently well constrained in either theoretical models or laboratory experiments. In particular, there are wide discrepancies in the predicted amount of H_2 that will be generated through the oxidation of Fe during olivine and pyroxene hydration and carbonation. Geologically-produced H_2 gas is of interest because it can drive the biological and/or abiotic synthesis of methane and low molecular weight organics, and the concomitant utilization of CO_2, depending upon the geological conditions. Alternatively, dissolved CO_2 may be significantly consumed in mineral carbonation reactions that not only suppress H_2 generation, but result in the formation of stable metal carbonates. The overarching goal of this 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.

FY 2012 HIGHLIGHTS

In this first year of funding, we have successfully completed a series of experiments designed to measure the temporal evolution of H_2 from several geologically-relevant substrates (e.g., olivines, pyroxenes, and peridotites). To unravel the mechanisms of H_2 production, changes in the speciation of Fe in the primary and secondary mineral assemblage has been correlated with changes in pH_2, pCO_2, and aqueous Fe and Si activity. Our initial strategy for identifying the reaction products and changes in Fe speciation resulting from incipient water-rock interaction has utilized a newly established synchrotron x-ray based coupled multiple-energy microXRF and microXANES method to locate and identify both the rare and abundant Fe-bearing phases within complex samples (Mayhew et al., 2011). All of the water-rock reactions are thermodynamically predicted to result in H_2 generation; however, it is notable that the experiments that did produce H_2 were strongly correlated with the presence of trace spinel phases (e.g., magnetite, chromite, and gahnite) associated with the primary substrates. The dominant change in Fe speciation is the formation of Fe(III)-oxide layers on the spinel surfaces and the precipitation of Fe(II)-bearing talcs intimately associated with the pyroxene phases. We propose that low temperature H_2 generation is be significantly catalyzed by heterogeneous surface-mediated electron transfer reactions between Fe(II) and water molecules adsorbed to the surface of spinels. This first study has been submitted for publication (Mayhew et al., in review). Our work to-date sets the stage for several testable hypotheses regarding the rate and extent of geological H_2 generation in subsurface systems.

Multiscale Modeling of Dissolution in Rough Fractures

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

PROGRAM SCOPE

We are using a variety of numerical and analytical methods to investigate the dissolution of a single fracture. The knowledge obtained from these investigations will be used to construct a model for the change in fracture permeability during dissolution. Our goal is a model that incorporates the key feature of fracture dissolution—namely its strong spatial inhomogeneity—in a sufficiently simple way that it can be used to improve the accuracy of discrete fracture network models at the reservoir scale.

FY 2012 HIGHLIGHTS

We have finished an exhaustive analysis of the stability of reaction fronts in fractured and porous media. Our comprehensive study of fracture dissolution was published in the *Journal of Fluid Mechanics* [Syzmczak & Ladd, JFM 702, 239-264 (2012)]; and a companion paper on porous media is in preparation. We have also submitted a manuscript on reactive-infiltration instabilities in porous media to Physical Review Letters. It describes a common theoretical framework that provides a link between earlier theories while also delimiting their regions of applicability.

We have made a number of algorithmic advances in 2012, including a new lattice-Boltzmann code for porous media that is faster and uses less memory than previous versions. In addition, we have completed a code that can track the evolution of a three-dimensional pore space and provide the geometric input for lattice-Boltzmann simulations. Finally, we have compared different boundary conditions for lattice-Boltzmann simulations of reactive transport to determine the most accurate and efficient method for simulating the dissolution of fractures and porous-media.

Interface Induced Carbonate Mineralization: A Fundamental Geochemical Process Relevant to Carbon Sequestration

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

PROGRAM SCOPE

Carbonate minerals constitute the largest carbon reservoir in the global carbon budget and are the most abundant and reactive chemical/biochemical deposits at the Earth’s surface. The high reactivity ensures these minerals participate extensively in geochemical reactions at surficial and near-surface conditions.

Carbon's unique chemistry, embodied by the thermodynamic equilibria between CO_2 (g), HCO_3^- and $CO_3^=$ (aq), and solid phase carbonates, ultimately link these minerals to one of the most important environmental issues—the greenhouse effect.

Magnesium is the second most widely occurred metal component in carbonate minerals next only to calcium. However, low-T precipitation of Mg-rich carbonate phases dolomite ($CaMg(CO_3)_2$) and magnesite ($MgCO_3$) in lab settings has proven virtually impossible, posing a long-standing geochemical problem in carbonate mineralization. Rarely is there a geological puzzle that has endured as long a quest for solutions as this "dolomite problem" has. Low temperature reactions of Mg^{2+} with CO_3^{2-} yields exclusively hydrated or basic Mg-carbonates depending upon T, pH, and pCO_2 conditions, suggesting the close association of water with Mg ions that is believed retard $MgCO_3$ mineralization. Such understanding (i.e., cation hydration inhibits magnesite (and dolomite) formation) leads to an intriguing and yet fundamental question: *Will anhydrous Mg carbonate salts precipitate with ease if the water shells surrounding Mg^{2+} are replaced, for example, in a non-aqueous environment?* To the best of our knowledge, little information is available in the literature concerning carbonate mineralization in non-aqueous solutions. In this project, we attempted to test the long-standing hydration retardation hypothesis through exploring the possibility of synthesizing magnesite and dolomite in water-free solvent at ambient conditions.

FY 2012 HIGHLIGHTS

We performed synthesis of $MgCO_3$ and $Mg_xCa_{(1-x)}CO_3$ ($0 < x < 1$) solid phases at ambient conditions in formamide that resembles water in density, polarity, and surface tension, but with a much weaker hydrogen bonding due to the stronger steric effect. Experiments results showed that, although anhydrous phases are readily precipitated in the water-free environment, the precipitates' crystallinity is highly dependent of the Mg mol% content in the solution. Pure-Mg and high-$[Mg^{2+}]/[Ca^{2+}]$ solutions produced exclusively amorphous phases of $MgCO_3$ or $Mg_xCa_{(1-x)}CO_3$, whereas proto-dolomite of moderate crystallinity was precipitated at $[Mg^{2+}]/[Ca^{2+}] = 1$ conditions and magnesian calcite of good crystallinity was formed in low $[Mg^{2+}]/[Ca^{2+}]$ solutions. These findings exposed a previously unrecognized intrinsic barrier for Mg^{2+} and CO_3^{2-} to develop long-range orders at ambient conditions, and suggested that the long-held belief of cation-hydration inhibition on dolomite and magnesite mineralization needed to be reevaluated. Our study provides significant insight into the long-standing "dolomite problem" in geochemistry and mineralogy, and may promote a better understanding of the fundamental chemistry in biomineralization and mineral-carbonation processes.

Development of New Biomarkers for Surficial Earth Processes

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Funding:	$147,000

PROGRAM SCOPE

During the current grant period, we engineered growth chambers that feature enhanced dynamic stabilization of moisture availability and relative humidity, as well as provided constant light, nutrient, $\delta^{13}C_{CO2}$, and pCO_2 levels for up to four weeks of plant growth. An unprecedented level of environmental stabilization allowed us to quantify the fundamental relationship between pCO_2 and carbon isotope fractionation in C_3 land plants, and we report upon a total of 191 C_3 plants (128 *Raphanus sativus* plants and 63 *Arabidopsis thaliana*) grown across fifteen different levels of pCO_2, ranging from 370 to 4200 ppm. From each plant, we isolated several substrates for carbon isotope analysis, including leaf-extracted nC_{31}-alkanes, a specific compound commonly isolated from terrestrial sediments of various ages. All of our substrates showed an increase in carbon isotope discrimination ($\Delta\delta^{13}C$) with increasing pCO_2 that closely fitted (i.e., $R \geq 0.94$) the hyperbolic relationship:

$$\Delta\delta^{13}C = [(A)(B)(pCO_2 + C)] / [A + (B)(pCO_2 + C)] \quad (1)$$

where A is the asymptote; B is a measure of the responsiveness; pCO_2 is offset by the value C, such that $\Delta\delta^{13}C = 4.4‰$ at $pCO_2 = 0$ ppm. Values for A and B were determined by iterative optimization to minimize the sum of the residuals squares. On the basis of our experiments on *A. thaliana* and *R. sativus* as well as published data across small changes (<350 ppm) in pCO_2, we optimized the variables in Equation 1 to produce a single equation describing the relationship between $\Delta\delta^{13}C$ and pCO_2:

$$\Delta\delta^{13}C = [(28.26)(0.21)(pCO_2 + 25)] / [28.26 + (0.21)(pCO_2 + 25)] \quad (2)$$

FY 2012 HIGHLIGHTS

This quantification of the pCO_2-dependency of carbon isotopic fractionation during photosynthesis has far-reaching ramifications for the interpretation of carbon isotope measurements in terrestrial C_{org}, and we wish to use renewal funding to pursue the five that are most important. Because of design limitations inherent to our growth chambers, our work-to-date has not explored the isotopic relationship between plant tissues and subambient pCO_2: Project 1 proposes to build low-pCO_2 growth chambers and conduct experiments across a range of subambient levels (approximately 200 – 350 ppm). Projects 2 – 4 are designed to quantify the effect of the pCO_2-dependency upon each of the three interpretations commonly invoked to explain changes in the $\delta^{13}C$ of terrestrial C_{org} within the sedimentary record. Finally, Equation 2 suggests that $\Delta\delta^{13}C$ (as defined above) can be used to solve for pCO_2: Project 5 details the assumptions and conditions necessary for this calculation, and evaluates the $\delta^{13}C$ of fern *n*-alkanes as an ideal proxy, given their abundance in the fossil record, particularly during the Paleozoic.

Field-Constrained Quantitative Model of the Origin of Microbial and Geochemical Zoning in a Confined Fresh-Water Aquifer

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Funding:	$125,000

PROGRAM SCOPE

The goal of this project was to develop, using techniques of molecular biology and on the basis of rigorous quantitative analysis, an improved understanding of the relationship between the chemical composition of groundwater in an aquifer and the microbial community there. Key questions to be addressed by this research include (1) *In what ways does microbial activity affect the chemical* *composition of groundwater?* (2) *How does groundwater composition affect the structure of the microbial community? What kinetic and thermodynamic factors in the subsurface control the rate of microbial activity?* (3) *How do the methods available to sample and observe the microbial community affect our knowledge of its nature?* (4) *What can reactive transport models tell us about the chemical evolution of groundwater flowing through biologically active aquifers?* The study used advanced techniques in molecular biology combined with in-situ sampling of attached microorganisms and dissolved gas concentrations to address these questions using groundwater sampled from wells in the Mahomet Aquifer, the regional water supply for central Illinois. The study integrated results of benchtop column experiments and a field study to inform numerical biogeochemical modeling efforts.

FY 2012 HIGHLIGHTS

We found that the communities of attached and suspended microbes in an aquifer vary depending on the concentrations of sulfate, methane, and ferrous iron. A statistical comparison of the community profiles revealed systematic similarities and differences in the bacterial communities between sites with high and low sulfate concentrations. Examining 16S rRNA gene clones, we found the relative proportion of bacterial populations associated with iron reduction appeared to increase with lower sulfate concentrations. To obtain real rate data, we have focused on bacterial mediated sulfate reduction. Using a novel bioreactor design, we tested sulfate reduction rates 300 times lower than previously tested. We found that the relative *dsr*A transcript per cell decreases proportionally with the rate of sulfate reduction. We have developed numerical models of the origin of microbiological zoning in groundwater flows, based on principles of thermodynamics, kinetics, and population ecology. The modeling shows neither thermodynamic nor simple kinetic interpretations explain the mechanism by a microbial population excludes others from a zone. Instead, microbes in the models exclude competitors by maintaining conditions under which growth of other populations is insufficient to replace cells lost to decay and predation. The models show that communities assumed to be dominated by a single functional group may in fact be areas of mixed metabolism. For example, zones containing iron-rich groundwater may be dominated by sulfate reducing bacteria rather than iron reducers, and thermodynamically, we predict a mutualistic relationship may exist between these two types of metabolisms.

Mineral-Fluid Interactions: Synchrotron Radiation Studies at the Advanced Photon Source

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PROGRAM SCOPE

Structure and reactivity at the mineral-fluid interface are beginning to be understood for some of the most common minerals, and further progress is limited in part by the development of new experimental and computational techniques capable of elucidating the atomic realm. Much of the recent work on mineral-fluid interfaces and mineral surfaces applies experimental and theoretical techniques and approaches used by scientists studying other types of materials (e.g., catalysts and semiconductors) in the surface chemistry and materials science communities. A particularly powerful set of techniques for studying surfaces, thin films, and interfaces arises from x-ray scattering effects, which become practical for in situ mineral-water interface studies only at high-intensity synchrotron radiation sources. These x-ray scattering techniques had not been applied to in situ studies of mineral-fluid interfaces before our group at Argonne and UIC began developing such applications at the National Synchrotron Light Source in 1992. We have performed experiments at the Advanced Photon Source (APS) since late 1997. These experiments demonstrated the first uses of low-angle x-ray reflectivity, thin-film diffraction, x-ray standing waves, crystal truncation rods, resonant anomalous x-ray diffraction (RAXR), and x-ray reflection interface microscopy measurements for high-resolution in situ studies of mineral-fluid interfaces in static and dynamic mineral-fluid systems. We are focusing our efforts in several experimental systems, each corresponding to a major area of scientific need in mineral-fluid interface studies, by combining synchrotron methods with atomic-force microscopy and other complementary methods to better understand the relations between structure and reactivity and as rock-forming minerals interact with crustal fluids.

FY 2012 HIGHLIGHTS

We performed a reanalysis of the structure of the calcite (104) – water interface using specular x-ray reflectivity at a vertical resolution of 0.45 Ångströms. These new data show two organized interfacial water layers, consistent with previous results, and distortion of the interfacial calcite structure to a depth of four to six unit cells, at least two deeper than previously reported. These results are in reasonable agreement with recent computational studies in terms of the locations of the first and second water layers but reveal new features not captured by either of these models or by previous x-ray reflectivity results. In addition, we have performed experiments on incorporation of Pb by the calcite (104) surface in contact with ~0.1 mM Pb-EDTA solutions using in situ RAXR to determine the distribution of Pb with depth in the calcite lattice. Lead occupies ~24% of the top unit-cell layer Ca sites, with decreasing occupancies at depth (from ~8% in the 2nd layer to ~2% in the 5th layer). Atomic-force microscopy indicates a dissolution-reprecipitation mechanism for Pb incorporation in calcite.

Shale Gas: Geochemical and Physical Constraints on Genesis, Storage, and Producibility

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Funding:	$216,000

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) natural outgassing of methane from shales into the atmosphere and its potential contribution to global warming by delivering potent methane greenhouse gas; and (3) isotopic testing of shales’ ability to generate catalytic gas at relatively low temperature, without the presence of methanogenic microbes.

FY 2012 HIGHLIGHTS

Porosity in shales was determined to strongly depend on the presence of organic matter and its thermal maturity. Porosity in shale 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 effectively reduces the 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. Two papers related to this aspect of the project have already been published (one in *Energy & Fuels*, and one in the *International Journal of Coal Geology*) and another manuscript is being submitted to the *AAPG Bulletin*.

Natural outgassing of methane from shale gas into the atmosphere in the absence of drilling and fracking was evaluated on numerous field trips to New York, Pennsylvania, Kentucky, and Indiana. A naturally occurring 'eternal flame' and associated shale gas seeps in Chestnut Ridge County Park (Erie County, New York) are fed along fractures by gas from Devonian shales. The gas has unusual chemical and isotopic compositions and will be described in a publication that also characterizes another 'eternal flame' from Pennsylvania. The occurrence of gas seeps fed by deeper shales proves that strong fluxes and point sources of shale gas can indeed contribute to atmospheric greenhouse gas loading. However, we found no strong evidence that small natural fluxes of shale gas deliver methane to the atmosphere. Limestone caves in Kentucky and Indiana are overlying deeper shales and were expected to accumulate methane in cave air if fractures in deeper rock permit upward flux of shale gas. Instead, we typically found less methane in cave air than in the atmosphere. We hypothesize that methanotrophic microbes are lining the surfaces of underground gas passageways and oxidize the methane from shale gas to carbon dioxide before methane can reach the atmosphere.

Crystal Chemistry of Toxic Metal Sequestration

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Funding:	$224,000

PROGRAM SCOPE

This project involves development and application of integrated imaging, spectroscopic, and scattering methods to uranium contaminated soils. The project centers on the crystal chemistry of minerals that host toxic metals in contaminated environments. The current focus is on investigation of uranium sequestration by adsorption on surfaces and incorporation within mineral hosts using TEM, FIB, neutron scattering, and synchrotron-based techniques.

FY 2012 HIGHLIGHTS

This year has included significant advances in understanding the phase transitions in uranyl phosphates of the autunite group. This work includes development of an in situ cell for synchrotron x-ray powder diffraction at the GSECARS Sector 13 beam line of the Advanced Photon Source. The cell utilizes gas mixing, microheaters, and relative humidity sensors to control and monitor temperature/a_{H2O} relations of dehydration reactions in the series. Preliminary results with the cell show that the temperature and kinetics of transition for the Cu uranyl phosphate mineral metatorbernite are highly sensitive to a_{H2O} and are reversible. We have also succeeded in synthesizing deuterated analogs of meta-autunite group minerals to facilitate investigation with neutron scattering. We are currently using neutron data for metatorbernite to probe the positions of light elements in the interlayer.

Predictive Surface Complexation Modeling

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Funding:	$141,000

PROGRAM SCOPE

Three overall goals have been proposed: (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. By so doing, the proposed research aims to integrate the results of the work of many experimentalists and to extrapolate their work to provide estimates of surface chemistry for systems not yet studied experimentally and for natural and anthropogenically perturbed systems.

FY 2012 HIGHLIGHTS

Tests of predictive surface complexation modeling are crucial to establishing the credibility of the predictive capability. For organic molecules interacting with mineral surfaces, tests can be made using in situ spectroscopic techniques. Previously, we and many others have used Fourier transform infrared spectroscopy (FTIR). However, the effects of surface attachment in FTIR are subtle because signal can arise not only from the species attached to the mineral surface but also from water and species in aqueous solution. In contrast, surface-enhanced Raman spectroscopy (SERS) is extremely sensitive to the adsorbed species only. We have carried out the first SERS study of an organic molecule on a mineral surface under different pH and surface coverage conditions. The Raman signal enhancement arises when a charge transfer (CT) complex forms between our TiO_2 nanoparticles and an adsorbed amino acid dihydroxyphenylalanine (DOPA). This Raman signal is exclusively from the surface-bound complexes with great sensitivity to the binding and orientation of the DOPA attached to the TiO_2 surface. Our SERS spectra show peaks that progressively change with pH and surface coverage, indicating changing surface speciation. At low pH and surface coverage, DOPA adsorbs on the surface lying down, with probably three points of attachment, whereas at higher pH and surface coverage, DOPA stands up on the surface as a species involving two attachment points via the two phenolic oxygens. Our results demonstrate experimentally the varying proportions of the two surface species as a function of environmental conditions. The results are closely consistent with our previously published surface complexation modeling of DOPA on TiO_2.

Lee, N., Hummer, D. R., Sverjensky, D. A., Rajh, T., Hazen, R. M., Steele, A., and Cody, G. D., 2012. Speciation of l-DOPA on Nanorutile as a Function of pH and Surface Coverage Using Surface-Enhanced Raman Spectroscopy (SERS). *Langmuir*, 10.1021/la303607a, Nov. 19.

Collaborative Research: Evolution of Pore Structure and Permeability of Rocks Under Hydrothermal Conditions

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

PROGRAM SCOPE

The transport properties of rocks can be altered by diagenetic, metamorphic, and tectonic processes. Such changes are critically important to the understanding of industrial applications including resource recovery, carbon-dioxide sequestration, and waste isolation, and natural processes, including metamorphism, fault mechanics, and pressure solution. Here, we propose to investigate the changes of permeability and pore geometry owing to inelastic deformation by solution-transfer, brittle fracturing, and dislocation creep in fluid-filled quartz and calcite rocks and to investigate the effects of loading configuration on porosity and permeability under hydrothermal conditions. We will perform laboratory experiments, numerical calculations, and observations of microstructure. The experiments provide mechanical and transport data under conditions designed to isolate each particular mechanism. The data will be used in network, finite-difference and other numerical models to elucidate relations between permeability and other rock properties.

FY 2012 HIGHLIGHTS

Power-law relationships are widely used to relate permeability to porosity. The power law exponent, α, quantifies the dependence of permeability on changes in porosity, with higher α values indicating a greater change in permeability for a given porosity change. Previous studies show that α is sensitive to pore geometry and varies significantly at different mechanical, thermal and chemical conditions. In fact, α may be a diagnostic indicator of the pore evolution process [Zhu et al., 2007; Gribbin et al., 2012]. We measured the permeability and porosity of massive anhydrite deposits recovered from several seafloor hydrothermal vent fields. This sample suite is composed of anhydrite rocks that have undergone different stages of anhydrite precipitation and dissolution. Interestingly, there are two different permeability-porosity relationships in anhydrite samples with high or low porosity. Petrography shows that dissolution and precipitation coexist in these deposits and suggests that the pore-evolution processes are sensitive to pore size. Precipitation of anhydrite takes place preferentially in large vugs within the anhydrite structure but is limited in smaller pores. The permeability-porosity trends reflect this interplay between dissolution and precipitation. At high porosities, α~9 is found. The abundant vugs are ideal sites for the growth of secondary anhydrite, resulting in drastic permeability decreases due to loss of pore connectivity. At low porosities, while precipitation continues in larger pores, population of small pores grows considerably due to precipitation of both secondary anhydrite and sulfides. Enhanced dissolution in small pores likely keeps fluid paths open; and, thus, a gradual reduction in permeability is observed (α~1). This permeability-porosity relationship in anhydrite deposits is in stark contrast to that seen in samples of Fontainebleau sandstone, a quartz arenite with various degrees of cementation. Rocks from that formation show a gentle permeability-porosity trend, α~3, at high porosities, but a much steeper trend at lower porosities, α~8. Identifying the contributions of these processes to changes in the pore structure of anhydrite deposits is a necessary step for refining fluid feedback models. We are currently preparing a manuscript for publication.

Collaborative Research: Evolution of Pore Structure and Permeability of Rocks Under Hydrothermal Conditions

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

PROGRAM SCOPE

The transport properties of rocks can be altered by diagenetic, metamorphic, and tectonic processes. Such changes are critically important to understanding engineering applications—resource recovery, carbon-dioxide sequestration, and waste isolation—and natural processes—metamorphism, fault mechanics, and pressure solution. In this project, we investigated the changes of permeability and pore geometry owing to inelastic deformation by solution-transfer, brittle fracturing, and dislocation creep in fluid-filled quartz and calcite rocks and the effect of changes in loading configuration on permeability evolution under hydrothermal conditions. Laboratory experiments provide mechanical and transport data under conditions designed to isolate each particular mechanism. Simultaneous measurements of pore volume, permeability, axial, and volumetric strain rates have been made under isostatic and conventional triaxial loading at temperatures up to 800 K, with confining pressure and pore pressures maintained independently up to 500 MPa. Scanning electron microscopes and laser confocal scanning optical microscopes are used to examine surface roughness, porosity, and pore dimensions. These data are used to constrain network, finite-difference, and other numerical models.

FY 2012 HIGHLIGHTS

With S. H. Hickman and N. Beeler, USGS, Menlo Park, CA., we measured deformation at a single contact between a curved mineral lens and a flat mineral substrate, to accuracies greater than 1 nm/hr. The contacts were rough, being composed of pillars 1-10 µm wide and 0.1-0.2 µm deep. Three modes of behavior occurred: (1) healing with no convergence, (2) fracturing of the pillars, and (3) pressure solution at the contact. To complement the experiments, we simulated creep of a three-dimensional, randomly packed assemblage of quartz spheres using a distinct element method of *Cundall and Strack* and constitutive behavior suggested by *Lehner and Leroy*. During long duration simulations with T between 773 and 973°K and p_c from 40 to 120 MPa, the grain-contact coordination number grew to values approaching 10, causing very large decreases of the mean contact force and considerable increases of the bulk modulus. Strain was proportional to t at early times (i.e., less than 0.1 year), but depended on $t^{1/2}$ at late times (<1000 years). In another study, we determined that the effective pressure law (EPL) for permeability in tight sandstones from reservoirs in China was non-linear, an important implication for models of reservoir permeability and for predictions of the reservoir evolution during oil and gas production. Finally, we studied the effect of pore connectivity and heterogeneity on permeability using a set of network simulations, and found that the permeability and formation factor of the networks were well approximated by the power laws of $(z\text{-}z_c)$, where z_c is the critical coordination number at the percolation threshold.

Early Career - Nonequilibrium Physics and Phase-Field Modeling of Multiphase Flow in Porous Media

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Funding:	$150,000

PROGRAM SCOPE

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: (1) immiscible fluid displacements in a Hele-Shaw cell, (2) multiphase flow in porous media, and (3) application to CO_2 storage in saline aquifers. If successful, this proposal will provide a continuum mathematical framework that predicts the stability—instability of fluid displacement at large scales. This would be a landmark result in soft-matter physics, leading to fundamental advances in the deployment of energy systems (oil and gas recovery, CO_2 sequestration, fuel cells, microfluidics) that depend crucially on the formation and control of fluid-fluid instabilities.

FY 2012 HIGHLIGHTS

We have developed a new model of two-phase flow in a capillary tube in the partial-wetting regime. The new model emerges from thermodynamic considerations and enjoys the remarkable feature that it leads, under static conditions, to the formation of compactons (compactly-supported structures at rest, like bubbles and slugs). The model also reproduces the dynamic behavior of two-phase flow, such as the dependence on the capillary number of the dynamic contact angle and the thickness of the liquid film left at the tube walls. We have published this work in Physical Review Letters.

We have also extended the phase-field model to modeling the formation of puddles (compact structures in two dimensions). The model predicts a transition from a connected to a disconnected liquid phase on a partially-wetting substrate, including the formation of labyrinthic structures, depending on the static contact angle and the initial height of the puddle. Our modeling approach also permits, for the first time, modeling the linear and nonlinear stability of thin film flows without precursor films.

Physics of Channelization: Theory, Experiment, and Observation

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Funding:	$142,000

PROGRAM SCOPE

We study the growth of channel networks incised by groundwater flow. The objective is to quantitatively relate mechanisms of growth to network geometry. We focus on the growth and bifurcation of channel tips. Our investigations involve physical reasoning, mathematical and numerical modeling, and empirical analysis of a 100-km^2 channel network on the Florida Panhandle. We also explore ways in which our theoretical insights can be applied more widely to channel networks formed in different environments.

FY 2012 HIGHLIGHTS

Our work during FY 2012 has focused on the geometry and dynamics of ramification—the mechanism of branching by which networks grow. We find that the Florida network grows in response to the surrounding groundwater field, with a specific geometric signature that is independent of the mechanisms of sediment transport within streams. To obtain this result, we have coupled a classical model of groundwater hydrology to the simple hypothesis that channels grow in the direction from which groundwater enters their tips. We then solve for the angle at which a split tip grows without curving. This constraint—essentially a requirement that growth is self-similar—predicts that the opening angle between branches equals $2\pi/5 = 72°$. To test this theory, we have extracted the locations of thousands of bifurcated streams from a high-resolution topographic map of the Florida network. The resulting histogram of 4966 bifurcation angles yields a mean angle of $71.9° \pm 0.8°$, unambiguously consistent with our theoretical prediction.

We are currently focusing on dynamical aspects of tip splitting. One hypothesis suggests that tips split when the water table in front of a tip develops two maxima, thereby providing two directions of growth. We have formulated this hypothesis as a numerical model, and are in the process of comparing model predictions against reconstructions of the growth of the Florida network.

Rheological Properties of Earth's Upper Mantle at High Pressure: Roles of Melt, Water and Pressure

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Funding:	$93,000

PROGRAM SCOPE

Our project is an experimental approach to relevant Earth problems involving the flow of olivine-rich rocks in the upper mantle. It is a collaborative effort with the University of Minnesota, David Kohlstedt, PI, whose Abstract also appears here. Using the deformation-DIA (D-DIA), an advanced high-pressure, high-temperature deformation instrument, we investigate the influence of pressure on the rheological properties of mantle rocks. We measure both the direct effect of pressure through its influence on activation enthalpy via the classic PV* (pressure times activation volume) term as well as the indirect effect of pressure through its influence on melt distribution in partially molten rocks and on water concentration within mineral grains and along grain boundaries under hydrous conditions. Measurements of stress and deformation rate, which together constitute the basic flow relation we seek, are carried out on samples inside the D-DIA using x-ray synchrotron radiation, and are conducted at beam line X17B2 at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory.

FY 2012 HIGHLIGHTS

Influence of pressure on the creep of dry olivine: For this study, we conducted numerous deformation experiments on dry polycrystalline olivine in the D-DIA apparatus to pressures 1.5 to 9 GPa at 1373 K. Refinement of diffraction techniques now allows stress resolution of ±0.02 GPa. For the pressure range in this study, we have measured an activation volume $V^* = 14 \pm 3$ cm^3/mol for dry polycrystalline San Carlos olivine. This is a substantial pressure effect, representing a pressure-induced viscosity increase (all other conditions being equal) of seven orders of magnitude from the base of the lithosphere to the bottom of the upper mantle. The diffraction technique used for stress measurement in these experiments also illuminates the relative strength of differently oriented grains in our polycrystalline sample, providing new experimental evidence for preferred dislocation slip systems in olivine at high pressure.

FY 2012 highlights of our work on the behavior of olivine under hydrous conditions can be found in the Abstract of the same title contributed by University of Minnesota PI, David Kohlstedt.

Computational and Experimental Investigations of the Molecular Scale Structure and Dynamics of Geochemically Important Fluids and Mineral-Fluid Interfaces

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Funding:	$141,000

PROGRAM SCOPE

The principal objective of this joint research effort with Prof. Geoffrey Bowers of Alfred University is to improve molecular-scale understanding of the structure, dynamics, and reactivity of geochemically important fluids, fluid-mineral interfaces, confined fluids, and hydrous materials using computational chemical modeling and experimental methods sensitive to molecular-scale behavior, principally nuclear magnetic resonance spectroscopy. Molecular scale knowledge of the structure and dynamics of aqueous fluids, how these fluids are affected by mineral surfaces and molecular-scale nano-confinement, and how water molecules and dissolved species interact with mineral surfaces is essential to understanding the fundamental chemistry of a wide range of geochemical processes relevant to energy geoscience (e.g., contaminant storage and chemical transport in the environment). It is one of the most important cross-cutting fundamental research issues in effectively addressing the grand challenges in basic energy sciences.

FY 2012 HIGHLIGHTS

We have made significant progress in meeting each of these objectives. Our study of alkali metal and H_2O dynamics in expandable clay minerals discovered a new mechanism for the dynamics of H_2O molecules within 5 Å of a solid surface and was featured on the December 1, 2012, cover of the Journal of Physical Chemistry C. We also completed a study of comparable Ca-clays and observed the same type of dynamics. NMR relaxation data support the idea of GHz-scale librational motion along the H_2O C_2 symmetry axis. Novel ^{43}Ca NMR studies of Ca^{2+} in Ca-hectorite showed that Ca^{2+} follows our recently reported general relationship for cation dynamics in the alkali metal clays in which ion motion becomes progressively more dominated by isotropic 2D or 3D diffusion at lower temperature as ionic radius decreases and hydration energy increases. Manuscripts detailing this experimental work and parallel computational modeling showing the same mechanisms are currently in the final stages of preparation. Our group also broke new ground by performing systematic ^{43}Ca and ^{25}Mg NMR studies of ^{43}Ca-enriched ACMCs and related hydrated carbonates that provide new insight into the structure and molecular scale dynamics of these complex materials. We published one paper on this topic this year, and several are in preparation. Research results obtained during this past grant year also supported a successful peer-reviewed renewal of our science-theme proposal for high-field NMR, electron microscopy, and micro-XRD instrument time at Pacific Northwest National Laboratory for the remainder of the current grant and beyond.

Rheology of Earth's Interior: Experimental Investigation to Pressures of 15 GPa Using the Deformation-DIA

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Funding:	$226,000

PROGRAM SCOPE

The focus of this study is to quantify the rheological behavior of mantle rocks under simulated mantle conditions including experiments at high temperatures, at high pressures, and in the presence of fluid phases. The goal of our research is to assure that the flow laws determined in the lab are sufficiently robust to provide a basis for geodynamical models of mass and heat transport in Earth’s mantle.

FY 2012 HIGHLIGHTS

Influence of water on low-T plasticity of olivine*:* To quantify the influence of water on the flow behavior of olivine under lithospheric conditions, we carried out a series of experiments on the steady-state creep behavior of polycrystalline olivine under hydrous conditions at pressures of 4 to 6 GPa and temperatures of 673 to 1173 K. Experiments were performed using a deformation-DIA at the National Synchrotron Light Source at Brookhaven National Laboratory. Samples were fabricated from fine powdered San Carlos olivine under hydrous conditions. The low-temperature plasticity of olivine under hydrous conditions is constrained by our data to a value for the Peierls stress of 4.5 ± 0.3 GPa. This value for Peierls stress is significantly smaller than those reported for olivine under anhydrous conditions (6 -15 GPa) [Evans and Goetze, 1979; Raterron et al., 2004; Mei et al., 2010], indicating a significant influence of water on the low-temperature plasticity of olivine.

Influence of water on high-T creep of olivine*:* Creep experiments were conducted over a range of hydrous conditions to investigate the effect of water on the creep behavior of olivine at high temperatures and high pressures. Polycrystalline samples were deformed at $3 \leq P \leq 7$ GPa and $1273 \leq T \leq 1473$ K under hydrous conditions. After each run, water content in the deformed sample was determined using FTIR techniques. Water fugacity for the run was further computed using an established relationship between water content and water fugacity [Kohlstedt et al., 1996]. Based on those analyses, our results yield the dependence of creep rate of olivine on water fugacity to a power of

~1.5. These results provide a necessary constraint for modeling the dynamic activities occurring within Earth's interior, especially for those regions in which significant concentration of water exist, such as beneath a mid-ocean ridge and along a subducting slab.

Board on Earth Sciences and Resources

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Funding:	$100,000

PROGRAM SCOPE

The Board on Earth Sciences and Resources is the focal point for all Earth science-related activities at the National Research Council of the National Academies. The Board and its standing committees oversee and guide a range of projects and initiatives that provide independent, unbiased, scientific and engineering advice to the Nation on Earth science issues. The Board also coordinates U.S. participation in some international Earth science programs and activities. In response to requests, interests, and needs expressed by Congress, federal agencies, state agencies, the science community, the private sector, and others, the Board membership of distinguished experts convenes and facilitates meetings, studies, workshops, colloquia, and uses various communications tools to address Earth science topics with policy relevance. The Board's activities are focused on providing and communicating accurate and timely information to support decision making in government, industry, and academia and supporting exchange of information among scientists, engineers, and policy- and decision-makers.

FY 2012 HIGHLIGHTS

The Board on Earth Sciences and Resources and its five standing committees held ten meetings during Fiscal Year 2012 on topics including the efficiency of geotechnical systems, unconventional oil and gas, critical minerals, advances in volcanology research, river restoration through dam removal, and federal perspectives in Earth science research. Eight ad hoc study committees overseen by the Board and standing committees also released eight consensus study reports on topics including uranium mining, sea-level rise for the coasts of California, Oregon, and Washington, induced seismicity, international science at the U.S. Geological Survey, dam and levee safety, spatial data infrastructure, research opportunities in Earth science, and disaster resilience. The Board, together with its standing and ad hoc committees, has also overseen development of some enhanced communications initiatives including (1) short articles summarizing Board activities for various Earth science-related newsletters, the first of these will be released in an upcoming edition of NSF's EAR to the Ground; and (2) a video on sea-level rise for a general audience (based upon the sea-level rise report): http://dels.nas.edu/Materials/Videos/Sea-level-Rise.

A New Probe for Understanding Rock Elasticity - Time of Flight Modulation

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Funding:	$61,000

PROGRAM SCOPE

The non-Hooke's law and irreversible mechanical behavior of sandstone is explored in this project. The variation of these nonlinear effects with chemical environment and temperature are the main results we seek. Nonlinearity is an indicator of damage and of ultimate mechanical strength as well as dispersion, attenuation, and harmonic generation. We use high-frequency techniques employing resonances of samples to provide high-amplitude oscillations from moderate drives. The responses are measured either as whole-body changes to the resonances [nonlinear resonant ultrasound spectroscopy (NRUS)] or by localized measurements of the sound speed at some path through the sample [time-of-flight modulation (TOFM)]. In TOFM, a high-amplitude standing wave excites the sample while pulse travel times are measured transversely along the standing wave envelope. Altering the environment of the rock sample with water, carbon dioxide, and hydrocarbons provides data relevant to seismology and the stability of oil and gas formations.

FY 2012 HIGHLIGHTS

We are continuing our approach to understanding a “bare” porous rock network by removing all of the water. This is an extreme state, but it is to be both a platform for exploring the fundamental properties of the grain-plus-cement quartz/silica picture of sandstones and to provide a base to explore effects of adding chemical species to the sample. Our main experimental apparatus has been maintaining a 1-inch diameter core of Berea sandstone in vacuum – (better than 10^{-7} Torr) for over 20 months. Both the linear and nonlinear properties of this sample are still slowly changing after initial rapid changes in the first few months, with the appearance of anomalous softening at relatively low temperatures (~50C). Modeling these effects began this year using the finite element code COMSOL, which provides mode identifications suggesting previous analysis has not sufficiently included inhomogeneity and anisotropy. Longitudinal modes may interfere with unexpectedly close bending modes. We are developing models at both the sample scale and the grain scale. We are including grain rotation aided by a water-dependent term in the grain-boundary sliding of polycrystal cements. Berea is a commonly studied but complex sandstone. We believe the current changes are due to clay reservoirs releasing water. Over the next 1-2 months, we will be returning H_2O and CO_2 to this sample and measuring the results which will be input to the grain scale models. We then intend to instrument a core of clean sandstone (Fontainebleau) which will verify the models for the grain scale physics. Some work supported by this project appeared at the Fall AGU meeting and will appear in an upcoming book chapter (Eds. R. Guyer and A. Kim).

Complex Fluids in Self-Affine Fractures

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Funding: $138,000

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, and we will extend this technique to tight or obstructed fractures which are particularly susceptible to jamming. Preliminary results on jams which form near a single constriction in the pore space indicate, plausibly, that an imposed oscillation in the pressure gradient is most effective at releasing the jam. Furthermore, we observe that unusual correlated oscillations are present in the residual flow even under steady driving conditions.

FY 2012 HIGHLIGHTS

We have been analyzing the “channeling paths” displayed by fluid and suspended particles in transport through rough fractures. This study is preliminary to the principal focus of the project—the dynamics of particle clogging in transport—and is needed to characterize the effective geometry and flow fields in which particle motion is significant. The fracture surfaces are modeled as self-affine fractals so as to incorporate the properties of realistic subsurface fluid-solid interfaces. In agreement with earlier experimental and theoretical studies, we observe that such flows display prominent spatial heterogeneity, whereby the principal flux of fluid and particles is confined to fairly well-defined paths spanning the fracture.

Stress-Dependent Acoustic Propagation and Dissipation in Granular Materials

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Funding:	$127,000

PROGRAM SCOPE

The goal of this project is to develop a theoretical and experimental understanding of sound propagation, elasticity, and dissipation in granular materials. The topic is relevant for the efficient production of hydrocarbon and for identifying and characterizing the underground formation for storage of either CO_2 or nuclear waste material. Furthermore, understanding the basic properties of acoustic propagation in granular media is of importance not only to the energy industry but also to the pharmaceutical, chemical, and agricultural industries.

We employ a set of experimental, theoretical, and computational tools to develop a study of acoustics and dissipation in granular media. These include the concept effective mass of granular media, normal modes analysis, statistical mechanics frameworks, and numerical simulations based on Discrete Element Methods. Effective mass measurements allow us to study the mechanisms of the elastic response and attenuation of acoustic modes in granular media. We perform experiments and simulations under varying conditions, including humidity and vacuum, and different interparticle force-laws to develop a fundamental understanding of the mechanisms of damping and acoustic propagation in granular media. A theoretical statistical approach studies the necessary phase space of configurations in pressure, volume fraction to classify granular materials.

FY 2012 HIGHLIGHTS

We have developed a theory to predict the effective mass of granular media in terms the normal-mode spectrum of finite-sized granular systems. The theoretical formalism allows the interpretation of the effective mass experiments performed in our lab to perform a microscopic investigation of the origin of dissipation and elasticity properties in granular matter. The main goal is to derive expressions of the effective mass in terms of the complex valued normal modes of the confined granular medium. A pole-decomposition has been derived that allows us to obtain the normal mode spectrum from direct experimental measurement of the effective mass. The spectrum allows us to determine the precise dissipative properties of the medium. In a recent application, we have shown a marked increase of the damping rate of each normal mode with the humidity of the medium relevant to our measurements. We developed the theory for weakly and strongly damped medium to make contact with experimental results. This theory accurately predicts the frequencies, widths, and relative amplitudes of the various flexural mode resonances observed with rectangular bars, each having a cavity filled with loose tungsten granules. A set of computer simulations has been performed to test the theory and finds agreement with theoretical and experimental results.

Changes of Porosity, Permeability and Mechanical Strength Induced by Carbon Dioxide Sequestration

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Funding:	$210,000

PROGRAM SCOPE

The objective of this project is to conduct, in the context of CO_2 sequestration, a systematic investigation of how the flow of the acidic, CO_2 saturated, single phase component of the injected/sequestered fluid changes the microstructure, permeability, and strength of sedimentary rocks, specifically limestone and sandstone samples. The project consists of three tasks. (1) Continuous measurement of permeability versus time on core samples as CO_2 enriched brine is flowed through the sample. The kinetics of fluid-rock interaction and how it is controlled by various parameters will be investigated. (2) Correlation of porosity and permeability changes to before-and-after in the sample microstructure characterized via x-ray computed microtomography (microCT). (3) Measurement of mechanical properties of the limestone and sandstone samples that have been altered by injection and percolation of CO_2 are taken to investigate how mechanical failure is influenced by modification of the pore space.

FY 2012 HIGHLIGHTS

We are in the process of tackling the proposed experiments in porous sandstone and limestone. In expectation of the availability of samples that have been altered by injection and percolation of CO_2 for mechanical testing, we have undertaken a series of mechanical tests on limestone samples saturated with deionized water, which will provide data for latter comparison. A major challenge in characterizing the pore geometry of carbonate rock is its complexity. Nevertheless, microCT imaging has proved to be useful for characterizing the mechanical damage. Our new data revealed a significant reduction of the number of macropores in hydrostatically and triaxially compressed samples, as well as a decrease in the volume fraction of the microporosity backbone, with corresponding decrease in its thickness. We have developed reactive network flow models to study upscaling of reaction rates from pore-to-core scale. The current application has concentrated on reactions pertinent to CO_2 sequestration in sandstone deposits. We are currently building a dissolution model that accurately follows the geometry of the actively dissolving minerals. We are also developing a model for highly caustic solution flow through unconsolidated soils typical of the Hanford site. We have also extended a hybrid lattice Boltzmann/finite element scheme that was originally developed to calculate a homogenized effective permeability to also include the hybrid modeling of electrical conductivity and formation factor, which would allow one to consistently simulate the hydraulic and electrical transport using the multiscale method.

Reactivity of Iron Bearing Minerals and CO_2 Sequestration: A Multi-Disciplinary and Experimental Approach

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Funding:	$100,000

PROGRAM SCOPE

The primary goal of this research program is to understand the chemistry that results when supercritical CO_2 ($scCO_2$) with H_2S and/or SO_2 in deep saline formations (DFS) contact iron bearing minerals. Understanding the complexities the sulfur co-injectants introduce is a critical step in developing CO_2 sequestration as a climate-mitigating strategy. The research strategy is to determine the reactivity of different types of iron-bearing sandstones and compare these results to molecular-level studies using pure iron minerals conducted by collaborator Daniel Strongin at Temple University.

Research is investigating some of the complexity associated with CO_2 sequestration in DFS. Specifically, research is focused on developing an understanding of the chemistry that will result when $scCO_2$ with varying amounts of H_2S and/or SO_2 comes in contact with iron-bearing sediments common to DFS. A representative suite of well-characterized sedimentary rocks (sandstones, siltstones, marls, and carbonates) will be exposed to $scCO_2$, scCO2/H_2S, $scCO_2/SO_2$ as well as Na-Cl brines equilibrated with these supercritical fluids in a hydrothermal flow-through setup. The flow-through experiments are complemented with small-scale batch experiments. Mössbauer spectroscopy is used to investigate changes in iron mineralogy. This is complemented with Visible and Near Infrared spectroscopy and Fourier Transform Infrared spectroscopy.

FY 2012 HIGHLIGHTS

Research in the last funding cycle has focused on understanding the transformations of iron oxides and oxyhydroxides present in red and grey sandstones under a range of conditions simulating the environment near an injection plume, at the interface between the plume and DSF, and within a DSF near a plume. The results indicate that the iron minerals in both types of sandstones remain unreactive when exposed to $scCO_2$ comingled with water and either H_2S, SO_2, or H_2S and SO_2. However, in water-dominated systems, iron minerals (mostly hematite) contained in red sandstones are transformed into pyrite and/or siderite when exposed to H_2S or a combination of H_2S and SO_2. Exposure to SO_2 alone does not lead to conversion. Increasing the salt (NaCl) concentration in water-dominated systems promotes reactivity of iron minerals in red sandstones. Iron in grey sandstones remains largely unreactive regardless of experimental conditions.

Multiscale Modeling of Multiphase Flow, Transport and Reactions in Porous Medium Systems

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Funding:	$207,000

PROGRAM SCOPE

Our work is directed at constructing models of multiphase porous medium systems that are consistent across length scales. To ensure 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 (1) all macroscale variables are defined explicitly in terms of microscale properties; (2) closure relations are advanced that are consistent with the second law of thermodynamics; (3) models can be constructed at a range of length scales, up to the system scale; (4) hierarchical families of models can be developed with varying degrees of sophistication consistent with physical system of interest; and (5) 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 and transport model, (2) a two-fluid-phase flow and species transport model, and (3) reservoir scale models for the analysis of carbon sequestration. These objectives are supported by theoretical and computational work that is performed at the microscale and at the system scale.

FY 2012 HIGHLIGHTS

TCAT theory has been developed for several models. Over the last year the theory has been completed for transition regions between multiphase systems and single fluid systems, such as land-atmosphere boundaries. We have shown the advantages of TCAT compared to other averaging theories in terms of consistent descriptions of capillary pressure, the evolution of entity measures, such as specific interfacial areas and common curve lengths, and the description of solid behavior. We have advanced an adaptive Lattice Boltzmann algorithm for multiphase flow that has reduced simulation times by more than 90% compared to standard non-adaptive methods and is being used to simulate REV scale systems for capillary pressure, fluid saturation, interfacial areas, and common curve lengths. Theoretical analysis has been completed to derive reduced dimensionality models to describe carbon sequestration by averaging macroscale equations to the megascale in the vertical dimension.

The Influence of Reaction Pathways on the Reduction of U^{VI} to U^{IV}: The Role of the Intermediate U^{V} Species

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Funding:	$63,000

PROGRAM SCOPE

The focus of this project is to develop and apply rigorous *ab initio* theoretical methods for the analysis and interpretation of the core-level spectra of metal oxides and other ionic compounds. The systems of principle interest in the current period are U oxides with U(VI), U(V), and U(IV) oxidation states although other high spin metal oxides will be studied both for their own sake and because they aid our understanding of the UO_x systems. The long-term objective is to be able to deduce the character of the chemical interactions from the main and satellite peaks, especially for x-ray photoelectron spectroscopy (XPS). These theoretical efforts are coordinated with and carried out in collaboration with Dr. Eugene Ilton at PNNL. The theoretical simulations are based on wavefunctions built from fully relativistic four-component spinors and includes both scalar relativistic effects and the coupling of spin and orbital angular momenta, where the latter is essential for core-level spectroscopies as well as for heavy atoms. The wavefunctions take account of both one-body and many-body chemical and physical mechanisms that contribute to the often complex core-level spectra.

FY 2012 HIGHLIGHTS

The interpretation of XPS satellite structure as being due to “shake” processes has been placed on a sound level. It has been shown that shake has a more fundamental origin than the previously used interpretation in terms of charge transfer. In heavy metal oxides, the covalent interactions are so large that it is more appropriate to view the satellites as a form of shake from bonding to anti-bonding levels rather than as charge transfer. Quantitative methods to determine the extent of covalent character have been used to distinguish the bonding in actinide, lanthanide, and transition metal oxides. The XPS satellite intensity in different U oxides and in CeO_2 have been correctly related to the covalent character of the bond, thus extending the use of satellites to characterize the chemical state of an oxide. It has been shown that in order to fully understand the physical and chemical properties of actinide oxides, one must take the intermediate angular momentum coupling in the open 5f shell of actinide cations into account. Furthermore, this coupling is, to some extent, reflected in the XPS of these cations. An invited review, for *Surface Science Reports*, of the interpretation and meaning of XPS spectra is in the final stages of completion. In the next period, it is planned to examine mixed valence oxides and to extend the XPS analysis to capture the complimentary information contained in x-ray absorption spectra.

Collaborative Research: Nanopore Confinement of C-H-O Mixed-Volatile Fluids Relevant to Subsurface Energy Systems

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

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 hydrocarbon (HC) 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 (1) assess the adsorption-desorption behavior of methane and related HC volatiles (and their mixtures) on a variety of mineral substrates and in nanoporous matrices, (2) characterize the microstructure and dynamical behavior of methane and related HC volatiles at mineral surfaces and within nanopores with and without H_2O present at relevant P-T-x subsurface conditions, and (3) 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, Oklahoma University, 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 2012 HIGHLIGHTS

We have conducted a number of different kinds of experiments focusing on the behavior of propane, methane, or carbon dioxide interacting with different types of mesoporous matrices (e.g., SiO_2, TiO_2, ZrO_2). High temperature-high pressure gravimetric measurements on these fluids have revealed profound fluid densification in nanopores as the density (pressure) approaches that of the bulk critical density followed by a dramatic density decrease (fluid depletion). The CO_2 adsorption on TiO_2 has been modeled with density functional theory that employs a new version of the dispersion correction. Quasielastic neutron scattering experiments have been conducted at Oak Ridge National Laboratory on the system propane-mesoporous silica with or without CO_2 present. Results from these experiments are interpreted in terms of translational “diffusive” motion of propane, residence times between diffusion jumps, and the jump distances. Interestingly, the presence of CO_2 seems to enhance the mobility of propane in the mesopores. Preliminary NMR experiments have been conducted on the diffusion and relaxation behavior of water and methanol in mesoporous silica at ambient temperature but for pressures up to 250 MPa. In the case of water, we observe a pronounced decrease in the T_1 relaxation with increasing pressure.

Geochemistry of Interfaces: From Surfaces to Interlayers to Clusters

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Funding:	$90,000

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 2012 HIGHLIGHTS

Our research focuses on ion adsorption and the potential formation of ternary complexes between aqueous oxyanions (ClO_4^-, NO_3^-, SO_4^{2-}, SeO_3^{2-}, and SeO_4^{2-}) and mineral oxides such as silica (SiO_2) and hematite (α-Fe_2O_3) in the presence of aqueous alkaline earth metal (Mg^{2+}, Ca^{2+}) and heavy metal (Cd^{2+}, Co^{2+}) co-cations. To this end, total internal reflection-Raman (TIR-Raman) and vibrational sum-frequency generation (VSFG) spectroscopies provide complementary information on the oxyanion available binding modes (e.g., monodentate, bidentate). The strength of this approach is to provide a more complete molecular picture of oxyanion adsorption to mineral surfaces.

We have developed and custom-built a TIR-Raman spectroscopy setup for in situ investigation of mineral oxides/solution models. This instrument has allowed us to study specific vibrational modes of SO_4^{2-} ions adsorbed to silica and hematite-coated silica surfaces. From spectral analysis, we have shown that SO_4^{2-} adsorbs preferentially to these surfaces in a bidentate fashion. Moreover, with the addition of Mg^{2+}, Cd^{2+}, and Co^{2+} co-ions, we have observed a pH-dependent enhancement in SO_4^{2-} adsorption, thus indicative of the formation of ternary complexes. Finally, analysis of the asymmetric stretching sulfate (ν_{AS}-SO_4^{2-}) modes during dehydration of the hematite surface indicates that SO_4^{2-} inner-sphere adsorption onto the hematite surface occurs via a bidentate geometry.

Nanopore Confinement of C-H-O Mixed-Volatile Fluids Relevant to Subsurface Energy Systems

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Funding: $40,000

PROGRAM SCOPE

The goal of this project is to employ molecular dynamics approaches to understand the structure and dynamics of fluids containing hydrocarbons, water, and oxygenated compounds confined within narrow pores that could be found in sub-surface formations. The theoretical results are compared systematically to experimental data obtained by our collaborator David Cole of Ohio State University. The distinctive feature of this project is the inclusion of both organic and aqueous fluids. Immediate practical applications can be found in the design of environmentally benign fracturing fluids for hydrodynamic stimulation of shale formations.

Our contribution, based on atomistic simulations, will characterize fluids confined within alumina, carbon-based, and silica pores of various widths and geometries. The results will be comparable to neutron scattering and high-resolution x-ray reflectivity data. We will also determine the physical driving forces responsible for the phenomena observed, which might extend the applicability of our results to many other situations of practical interest (e.g., separation of water-ethanol mixtures).

FY 2012 HIGHLIGHTS

Our first publication has been highlighted in the cover art of the *Journal of Physical Chemistry C*. In this publication, we quantified how three metal oxide surfaces determine structure and dynamics of liquid water.

We are about to submit the second manuscript. In this report, we have determined how another hydrogen-binding fluid (ethanol) responds to an aluminum oxide surface. We have quantified hydrogen bonding networks, structure, and mobility. The results are in strikingly good agreement with sum frequency experimental data available in the literature.

The next step will consider mixtures of water and ethanol (or other short alcohols) as well as mixtures of water and methane (or other short hydrocarbons).

A. Phan, T. A. Ho, D. R. Cole, A. Striolo, "Molecular Structure and Dynamics in Thin Water Films at Metal Oxide Surfaces: Magnesium, Aluminum, and Silicon Oxide Surfaces," *Journal of Physical Chemistry C* 116 (2012) 15962-15973. Also featured in the *cover art* of *J. Phys. Chem. C*, volume 116, issue # 30, August 2nd, 2012.

A. Phan, D. R. Cole. A. Striolo, "Liquid Ethanol Simulated on Crystalline Alpha Alumina," *J. Phys. Chem. C* (2012) in preparation.

Physical Mechanisms Controlling CO_2-Brine Capillary Trapping in the Subsurface

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Funding:	$170,000

PROGRAM SCOPE

Capillary trapping of CO_2 in deep saline aquifers is a promising aspect in carbon capture and sequestration because it immobilizes CO_2 at the pore-scale and thus prevents large-scale movement of CO_2 within an aquifer. Compared to most current large-scale reservoir studies, this research project takes several steps back in scale to observe and model trapping at the pore-scale and to investigate how fundamental pore-scale processes translate into continuum scale properties that can subsequently improve the efficiency of physical trapping mechanisms at large spatiotemporal scales. The overarching hypothesis of the proposed research is that capillary pressure plays a significant role in capillary trapping of CO_2, especially during the water imbibition stage of the sequestration process. Our main questions, guiding the tasks of the proposed research, are as follows: *What is the morphology of capillary trapped CO_2 at the pore scale as a function of temperature, pressure, and brine concentration? How can we describe the capillary trapping in numerical models using formation-dependent but otherwise unique non-hysteretic continuum-scale functions of capillary pressure, interfacial area, and saturation? How do derived continuum-scale relationships compare with traditional models incorporating relative permeability hysteresis? How can trapped CO_2 volume be optimized via engineered injection and sweep strategies?* These questions will be addressed via high-resolution pore-scale imaging using synchrotron-based and conventional x-ray computed microtomography.

FY 2012 HIGHLIGHTS

We have established a laboratory setup for experimentation using supercritical CO_2 (elevated temperature and pressure) and will be conducting imaging experiments using this system at the Advanced Photon Source (April 3-4, 2013). Simultaneously, we have conducted capillary trapping experiments at ambient conditions using proxy fluids and simple pore geometries that have shown that non-wetting phase viscosity is the optimal variable to focus on for optimization of trapped CO_2 volume. Finally, capillary trapping experiments at ambient conditions using proxy fluids and natural rock samples (Bentheimer sandstone cores) have shown, via a topological analysis, that capillary trapping can be optimized on secondary imbibition by maximizing trapped non-wetting phase saturation after CO_2 injection. This suggest that CO_2 injection should be conducted at slow flow rates to drain as much of the brine from the pore space during injection and thereby maximize non-wetting phase connectivity.

An Investigation of Roughness and Weathering at the Bedrock-Regolith Interface

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Funding:	$230,000

PROGRAM SCOPE

We are investigating the interface where weathering occurs in rocks. Specifically, we are asking the question: *How can we predict and understand the roughness that forms at the interface between weathered regolith and unweathered bedrock, and how does this roughness relate to measured weathering advance rates?* This work is progressing at a variety of scales to develop models for interface evolution, rind formation, and weathering advance.

FY 2012 HIGHLIGHTS

To understand roughness at the mineral grain scale, we are developing our Ising model that treats surface topography. This model will likely help to elucidate neutron scattering data for weathered mineral surfaces. Neutron scattering data has been collected on weathered rock from Puerto Rico, Costa Rica, Virginia, and Pennsylvania. The observations are being investigated in terms of the effect of climate and lithology (shale, basaltic, granitic) on the weathering interface. The angular dependence of neutron scattering data is determined by the inhomogeneities that characterize the system. In particular, the correlation length—or statistical average distance of inhomogeneities—can be calculated from the scattering curves and is related to the fractal dimension.

At the clast to pedon scale, we have hypothesized that Fe-related chemolithoautotrophic microorganisms play a role in the disaggregation of intact bedrock to regolith. We tested this hypothesis in 9.2 m deep regolith developed in the Bisley watershed in Puerto Rico. Using metagenomics analysis tools, bacteria community composition and structure were assessed. Sub-phylum groups containing known iron-oxidizing microorganisms were found near the regolith-bedrock interface, consistent with chemolithoautotrophic bacteria playing an important role in disaggregation of bedrock.

At the pedon to landscape scale, we investigated controls on the depth of regolith formed on ridges of two rock compositions with similar initial porosities in Virginia (U.S.A.). We predicted that the regolith on diabase would be thicker than on granite because the dominant mineral (feldspar) in the diabase chemically weathers faster than its granitic counterpart. However, weathering advanced 20x deeper into the granite than the diabase and the plagioclase reaction front was 20x thicker. The 20x-discrepancy is explained mainly by connected micron-sized pores, as well as microfractures formed around oxidizing biotite at 20 m depth. Such porosity allows pervasive advection and oxidation reactions that may explain why the thickness of regolith worldwide on felsic rock is generally greater than on mafic rock. These observations elucidate the importance of fluid flow and oxidation reactions in controlling regolith.

Modified Invasion Percolation Models for Multiphase Processes

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

PROGRAM SCOPE

This research program is focused on improving understanding of multiphase fluid migration in permeable media at the pore-scale. The proposed work is outlined in the three subtasks listed below, each with an experimental and numerical component. This research initiative is conducted in collaboration with Sandia National Laboratories (SNL). The experimental effort is mainly based at Penn State University, while the numerical modeling is performed at SNL, both receiving mutual feedback.

Task 1: Introduce the effect of spatial variation of wettability (contact angle) on the development of modeled percolation paths in porous media of mixed wettability. A sequence of oil and water injections is performed on bead packs that have similar pore structures but different wettability characteristics. X-ray microtomography is used to visualize and analyze the fluid distribution in each bead pack at the end of fluid injection.

Task 2: Investigate the development and transitioning of preferential pathways for multiphase flow in porous media subject to stress and mechanical deformation. Current implementation with the fluid percolation models uses a static representation of the pore radii across the model domain. The experimental images will provide estimates of the change in total porosity for each change in effective stress, and the corresponding changes to the radii fields within the models will be constrained to reproduce the observed changes in overall porosity.

Task 3: Calibration of the percolation model to mimic dynamic flow processes such as diffusion and detachment of fluid fingering. Direct pore-scale visualization of trapped regions, fingers, and their corresponding interfacial areas relative to saturation and local pore size distributions will provide resource data for the validation of finger detachment in multiple pore-aperture configurations, primarily through measurement of fluid-fluid interfacial areas which currently show significant discrepancy between experiments and modeled percolation algorithms.

FY 2012 HIGHLIGHTS

The experimental component of task 1 has been completed, and we are on the design phase of task 2. MS student J. G. Celauro, who was appointed to research the team (task 1), completed all requirements for graduation in August 2012. An MS student from Penn State Schreyer Honors College, Victor Torrealba, is currently working on task 2. Preliminary findings were presented at Geosciences Symposium, Geophysical Properties and Processes, on April 5-6, 2012 in Gaithersburg Maryland. We also have one journal manuscript in review (Geofluids), and a second one in preparation.

The Physics of Swarms in Fracture Networks: Integration of Seismic Characterizaion and Controlled Micro-Transport

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Funding:	$148,000

PROGRAM SCOPE

The objective of this research is to achieve a physical understanding of how to control the injection and retrieval of advanced collaborative sensors within fractured networks. This will be the first application of the physics of swarms to fractures and fracture networks, and will have important implications for the future use of collaborative sensors to characterize the subsurface. A particle swarm is a dilute suspension of particles that exhibits collective behavior and remains a cohesive entity over long periods of time. The process by which a swarm forms depends on interparticle interactions and particle-wall interactions, particle size, number of particles, particle concentration, shape of the particles, and fluid velocities. Our *goal is to* explore the evolution, maintenance, and control of particles swarms in fractures over time to isolate the key features of the fractures that affect swarms, and to identify the dominant flow paths in fracture media using seismic methods.

FY 2012 HIGHLIGHTS

We determined that the localization and speed of particle swarms falling under the influence of gravity in uniform and variable aperture fractures depends on fracture aperture. Contrary to theories based on 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 of fracture aperture, the fracture surfaces maintain the swarm density through confinement that prevents expansion of the swarm and maintains the speed of transport. In a variable aperture fracture made from a cast of Austin Chalk, swarms were observed to accelerate and decelerate as the swarm passed through diverging and converging apertures. The variation in drag and confinement on the swarm from the fracture surfaces maintained the cohesiveness of the swarm and suppressed bifurcations two to three times during transport through the fracture.

Seismic detection of the dominant flow path in a fracture network requires a fundamental understanding of the seismic response of the fractures, fracture intersections, and the matrix that contains the fractures. From theory and experimental measurements, we determined that the existence of fracture interface waves masks the textural shear wave anisotropy of waves propagated parallel to the layering. We found that the orientation of a fracture relative to the layering can make a medium appear more isotropic or more anisotropic because of fractured-generated discrete modes. We also found that the intersection between two fractures support discrete-guided modes that are sensitive to the stress distribution along the intersections.

The Role of Water in Grain-Boundary Diffusion

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Funding:	$245,000

PROGRAM SCOPE

The textural and compositional evolution of polycrystalline materials is strongly controlled by an intricate set of kinetic feedback mechanisms that operate along grain boundaries in rocks. During the final months of the previous funding cycle (grain-boundary diffusion of incompatible elements), we explored isotopic fractionation by grain-boundary diffusion.

After grant renewal in 2012, we shifted our efforts to focus on the role of water in grain-boundary diffusion. Recent studies suggest that the presence of trace amounts of hydrous species in grain boundaries increased grain-boundary diffusivities by several orders of magnitude. This observation is significant because the *P–T* evolution of many solid-Earth systems likely occurred under hydrous, but water-undersaturated conditions. Almost all previous experimental studies of grain-boundary diffusion have investigated either ‘wet’ (free H_2O) or ‘dry’ systems; so our understanding of the effect of H_2O on grain-boundary diffusion is incomplete—especially in the commonplace H_2O-undersaturated regime. There is a general consensus that addition of water will enhance grain-boundary diffusivities, but there are no experimental studies that have systematically investigated the dependence on grain boundary ‘moisture’ content.

FY 2012 HIGHLIGHTS

Lithium isotopic fractionation by grain-boundary diffusion: Isotopes of an element may be fractionated by chemical diffusion. Diffusive fractionation of isotopes has been documented in silicate melts, aqueous fluids, and single crystals. In polycrystalline rocks, transport by grain boundary diffusion may also fractionate isotopes. We conducted a series of high *P–T* experiments to explore diffusive fractionation of Li isotopes by grain-boundary diffusion in polycrystalline aggregates of olivine (dunite). Diffusion couples were constructed by placing polished rock analogs directly against a Li diffusant source (spodumene) and running the diffusion couples in a piston-cylinder apparatus at high *P–T* conditions. During diffusion experiments, Li concentration gradients developed in polycrystalline dunites. Grain-boundary diffusion fractionated the Li isotopes near interfaces of the diffusion couples because the lighter ^{6}Li isotope diffused faster than the ^{7}Li isotope. Grain-boundary diffusive fractionation may significantly change the isotopic ratio of polycrystalline materials.

The role of water in grain-boundary diffusion: We are systematically exploring the role of water on grain-boundary diffusion. A variety of crystals and glasses were implanted with deuterium (a proxy for hydrogen that avoids environmental hydrogen artifacts related to experimental preparation) using a linear particle accelerator to produce deuterated materials for usage as ‘water’ bearing sources in diffusion experiments. These materials were placed against polycrystalline rock analogs and the diffusion couples were run at high *P–T* conditions. Infrared spectroscopy revealed that deuterium was present in the initially deuterium-free polycrystalline halves of the diffusion couples. The presence of deuterium in the polycrystalline rock analogs unequivocally demonstrates that deuterium was introduced by grain boundary diffusion.

Mechanisms of Pore Collapse in High-Porosity Rocks

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Funding:	$120,000

PROGRAM SCOPE

High-porosity rocks have the greatest potential to undergo irreversible compaction due to pore collapse instability. Reduction in rock porosity typically occurs from fluid extraction as fluid pressures decrease and loads are transferred as effective stresses into the mineral skeleton. Mechanisms of pore collapse include grain crushing (often termed cataclastic flow) and crystal plasticity in the mineral grains. In this project, we will develop a mesoscopic scale modeling approach to investigate the interplay between these two fine-scale processes as they impact pore collapse. We will model the solid matrix microstructure using the finite element method with the voids represented by hollow inclusions. Grain crushing will be represented by multiple slip surfaces through the solid matrix, and irreversible deformation in the mineral grains will be modeled using crystal plasticity theory. An assumed enhanced strain finite element formulation will be employed to enable the slip surface to pass through the interior of finite elements while keeping the grid fixed. All of these grain-scale mechanical processes will be homogenized to represent the overall mechanical response of a mesoscopic element, which, by definition, is intermediate between the specimen scale and grain scale. Based on this homogenized response, we will conduct bifurcation analyses at the mesoscopic scale to infer the onset of pore collapse instability at that scale. Laboratory-measured specimen responses will then be interpreted in the context of instabilities occurring in the mesoscopic level.

FY 2012 HIGHLIGHTS

We have looked into the effect of micro-structural inhomogeneity on the pore scale deformation of an idealized mesoscopic element of limestone. The pores are represented by cubic inclusions; the heterogeneity in the crystalline solid is represented in the form of inhomogeneous crystal orientation. As the meso-element deforms, we observed that crystal plasticity initiates near the imperfections in the microstructure. This informs us, among other things, about the delay in yielding of the mesoscopic element, characterized by a significant drop in the stress level as compared to the onset of plastic behavior in the microstructure. Thus, the seemingly linear elastic stress-strain response at the meso-scale cannot be interpreted as an absence of plasticity in the microstructure.

Porous Rock with Fluid: Impact of Heterogeneity and Scale on Relations between Rock Properties

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Funding: $252,000

PROGRAM SCOPE

This program focuses on performing digital and analytical experimentation to explore the scale dependence of relations between rocks' properties, such as porosity and permeability.

FY 2012 HIGHLIGHTS

(1) Macro-Scale Trends between Rock Properties. Arguably, it is impossible to address this question in the physical laboratory (most experimental systems are designed to accommodate fixed-size samples). Our trend upscaling research has used analytical and computational means. We have found, by using numerical Darcy's flow simulations, that some of the permeability-porosity trends obtained in the lab remain valid at a much larger scale.

(2) Experimental Work. We have prepared several artificial carbonate samples by mixing large calcite grains with very small micritic grains. These samples will be used to understand how the heterogeneity at the micro-scale affects the rock properties and relations between them.

Structural Heterogeneities and Paleo Fluid Flow in an Analog Sandstone Reservoir

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Funding: $295,000

PROGRAM SCOPE

The primary goal of the project is to develop conceptual and quantitative mechanical models and predictive tools for understanding the spatial distribution of permeability in subsurface sandstone aquifers and reservoirs as determined by structural heterogeneities. Many faults, fractures, and deformation bands are below seismic resolution but have a significant influence on fluid flow, acting either as conduits (open fractures) or barriers (low permeability fault rock, mineral-filled fractures, and deformation bands) to fluid transport. We are conducting a broad-based research project to map and characterize structural heterogeneities (deformation bands, joints, sheared joints, and faults) in the Jurassic Aztec Sandstone exposed at the Valley of Fire State Park, Nevada, as an analog for active reservoirs and aquifers. Our current efforts comprise complementary sub-projects: (1) orientation and distribution of compaction bands and the role of cross-bed orientation; (2) fluid flow through sandstones with intersection and overprinting structures such as compaction bands, joints, and faults; (3) modeling non-planar faults that can stick, slip, and open and the associated damage; and (4) modeling compaction and shear-enhanced deformation bands using Eshleby's model for inhomogeneous inclusions.

FY 2012 HIGHLIGHTS

Using a Discrete Feature Model, we analyzed fluid flow in 3D across a 20mx20mx5m volume of sandstone with multiset compaction bands and with compaction band arrays and intersecting joints and faults. The intersection angle of multiset compaction bands, and between joint sets and older compaction bands have strong effects on the up-scaled permeability tensor.

Using outcrop mapping, we distinguished three architectural categories of depositional and structural domains for the aeolian Aztec Sandstone at Valley of Fire, NV: (1) cross-beds with bed-parallel compaction bands, (2) cross-beds with high-angle compaction bands, and (3) cross-beds with both bed-parallel and high-angle compaction bands overlapping in a transition zone. This implies that mechanical anisotropy may play a significant role in the presence and orientation of compaction bands in aeolian sandstones.

We used a two-dimensional displacement discontinuity method with a complementarity algorithm to enforce contact boundary conditions and calculate conditions of stick, slip, and opening on geometrically irregular fault surfaces under tectonic loads. The opening and closing behavior of faults affects frictional resistance to slip; and perturbations in the local stress field are associated with off-fault damage, which has a significant effect on fluid flow.

We developed a MATLAB code for the quasi-static linear-elastic displacement, strain, and stress fields of an ellipsoidal inhomogeneous inclusion (Eshelby solution). We validated the code by comparing it to known analytical and numerical solutions, and applied it to evaluate the stress fields about compaction bands and shear enhanced compaction bands in the Aztec Sandstone.

Development of a Tender-Energy Microprobe for Geosciences at NSLS and NSLS-II

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Funding:	$113,000

PROGRAM SCOPE

The purpose of this project is to create a new, unique synchrotron-based user facility to examine geologic materials at the micron scale with a focused x-ray beam tuned specifically for lighter elements Na through Ti. This facility is designed and optimized for *tender* (1-8 keV energy) x-ray micro-spectroscopy and imaging applications for Geosciences research, and will complement existing *hard* x-ray facilities operating above about 4.5 keV. It will extend to lower energies the x-ray fluorescence (XRF) and x-ray absorption spectroscopy (XAS) capabilities typical of hard x-ray microprobes, as element-specific, non-invasive probes of elemental distribution, and local physical and electronic structures and states in crystalline and non-crystalline materials. In addition, it will offer advanced capabilities for microbeam extended x-ray absorption spectroscopy (EXAFS) for determination of more detailed local structure. This project will be undertaken by adding new micro-focusing capabilities at an established macro-focused (~1 mm spot size) tender-energy XAS beamline at X15B of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory, and will subsequently transition to the new tender energy spectroscopy (TES) beamline under development at NSLS-II. Its key attributes will be the distinct 1 to 8 keV energy range, user-tunable spot size, high flux and stability optimized for high-quality and extended XAS, options for both XRF and XAS mapping with rapid scanning, and a helium glove-box sample environment. Performance will improve when transferred to NSLS-II, a state-of-the-art new synchrotron designed for high brightness applications. The scope consists of design effort and equipment. The proposed microprobe does not yet exist as a whole, so individual components must be selected, customized, assembled, and integrated.

FY 2012 HIGHLIGHTS

Primary efforts in FY 2012 (project started in August) were to finalize specifications and place an order for the microfocusing KB mirror optics system. In addition, instrumentation control system design was addressed in collaboration with NSLS-II Controls Group staff. A meeting of scientific and technical advisors for this project was held in September.

Structural Basis for Stabilization and Transformation Behavior of Amorphous Calcium Carbonate

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

PROGRAM SCOPE

The main goals of this research program are to establish the role of structure in stabilization of amorphous calcium carbonate (ACC) and in the mechanism and kinetics of its transformation to crystalline forms. By establishing structure-stability relationships for ACC, we contribute to the foundation for predicting transformations in natural calcium carbonate systems and their importance in processes that govern cycling of carbon. Our focus is on model systems that have application to initial stages of calcium carbonate precipitation in terrestrial and marine systems, both inorganic and biogenic, as well as subsurface mineralization related to carbon dioxide sequestration. We also study natural biogenic ACC for comparison with model systems. In our work, we supplant traditional methods used for determining structure in crystalline materials by modern techniques suited for non-crystalline materials. We use synchrotron-based x-ray total scattering and x-ray absorption spectroscopy in combination with ^{1}H, ^{13}C, and ^{31}P NMR methods to assess short- and medium-range structure in ACC. These methods allow characterization of structural changes throughout the transformation of ACC into crystalline products, including calcite and vaterite, as well as the effects of dopants.

FY 2012 HIGHLIGHTS

We focused on three main topics: (1) characterization of the amorphous to crystalline transformation using in situ and ex situ methods, (2) structural changes accompanying dehydration of ACC, and

(3) comparison of structure in biogenic and synthetic ACC. For all topics, our studies have combined synchrotron-based x-ray pair distribution function analysis, x-ray absorption spectroscopy, and NMR methods to determine structural features of ACC and its transformation products. We find that ACC transformation in the presence of water vapor results in coeval formation of calcite and vaterite, in proportions that vary according to detailed environmental conditions. Our work on dehydration shows that only minimal changes occur in the calcium carbonate framework during water loss of up to 70%. We have established that the loss of water occurs among three different hydrous components, to different extents. Biogenic ACC, taken from gastroliths of marine crustaceans, shows short- and medium-range structure similar to that observed in hydrated synthetic ACC; however, significant difference are found in their hydrous components.

Reactivity of Iron-Bearing Minerals and CO_2 Sequestration: A Multi-Disciplinary Experimental Approach

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Funding:	$100,000

PROGRAM SCOPE

The primary goal of this research program is to understand the chemistry that results when supercritical CO_2 ($scCO_2$) with H_2S and/or SO_2 in deep saline formations (DFS) contact iron bearing minerals. Understanding the complexities the sulfur co-injectants introduce is a critical step in developing CO_2 sequestration as a climate-mitigating strategy. The research strategy is to understand macroscopic observations of this chemistry with an atomic/molecular level view using surface analytical techniques.

Research is investigating some of the complexity associated with CO_2 sequestration in DFS. Specifically, research is focused on developing an understanding of the chemistry that will result when $scCO_2$ with varying amounts of H_2S and/or SO_2 comes in contact with iron-bearing sediments common to DFS. A representative suite of well-characterized sedimentary rocks (sandstones, siltstones, marls, and carbonates) will be exposed to $scCO_2$, scCO2/H_2S, $scCO_2/SO_2$ as well as Na-Cl brines equilibrated with these supercritical fluids in a hydrothermal flow-through setup. The experimental system provides for long-term monitoring of changes in sulfur chemistry in the effluent. Complementary spectroscopic studies will use in situ vibrational spectroscopy to examine the interactions under near-field conditions at the molecular level and resolve the interaction of $scCO_2$, $scCO_2/H_2S$, and $scCO_2/SO_2$ with relevant iron mineral phases.

FY 2012 HIGHLIGHTS

Research in the last funding cycle has focused on understanding the transformations of iron oxides and oxyhydroxides to siderite ($FeCO_3$) in the presence of $scCO_2$ and aqueous sulfide. Techniques used were in situ attenuated total reflection Fourier transform infrared spectroscopy and ex situ x-ray diffraction. These in situ studies have concentrated on various ferric bearing mineral phases that included hematite, and a series of crystalline iron oxyhydroxides (goethite, lepidocrocite, and akaganeite). To date, we have shown the conditions under which carbonate can be mineralized via reactions with iron oxides and iron oxyhydroxides under conditions relevant to subsurface CO_2 sequestration conditions.

Time-Lapse Seismic Monitoring and Performance Assessment of CO_2 Sequestration in Hydrocarbon Reservoirs

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Funding:	$228,000

PROGRAM SCOPE

The goal of this project is to examine the viability of time-lapse seismic monitoring using an integrated modeling of fluid flow, including chemical reactions, geomechanical effects, and seismic response. A critical aspect here is computational efficiency so that the approach can be suitable for large-scale field applications using high resolution geologic and seismic models. Our work focuses on fully integrating fluid flow and seismic data for monitoring injected CO_2 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 streamline-based compositional modeling of CO_2 sequestration, including compressibility, stress-sensitivity, compositional, and geochemical effects. For data integration and uncertainty assessment, we adopt an efficient Bayesian framework using multistage Markov Chain Monte Carlo (MCMC) methods.

FY 2012 HIGHLIGHTS

We have introduced a novel parameterization approach to mitigate the challenges associated with field-scale calibration of geologic models to time-lapse seismic data. The reservoir property field is mapped to and updated in a low-dimensional transform domain using a linear transformation basis. The transformation basis vectors are the eigenvectors of a Laplacian matrix that is constructed using grid connectivity information and the main features in a given prior model. We generalized previous formulations of streamline-based seismic inversion to incorporate realistic field situations such as changing boundary conditions due to infill drilling and pattern conversion. A robust and easy-to-implement streamline tracing algorithm for use in polygonal cells based upon cell face fluxes has been developed. Our proposed solution relies upon a refinement of the polygonal cells and provides a velocity field which is locally conservative, allows analytic calculation of the streamline trajectories, and does not require knowledge of the sub-cell permeability tensor or transmissibilities. We extend these results to support convex, nearly degenerate, and non-convex polygons as may arise for complex grid geometries associated with faults and grids with local grid refinement. [Rey, A., Bhark, E., Gao, K., Datta-Gupta, A. and Gibson, R., “Streamline-based integration of time-lapse seismic and production data into petroleum reservoir models,” *Geophysics*, 77 (6), (2012).]

Geochemistry of Interfaces: From Surfaces to Interlayers to Clusters

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Funding: $91,000

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 2012 HIGHLIGHTS

Cd^{2+}, Pb^{2+}, and SeO_3^{2-} adsorption onto goethite was successfully modeled in single and bi-solute systems using charge distribution multi-site complexation (CD-MUSIC). Goethite's crystal face composition was determined using the new modified titration congruency method (MTCM), which utilizes surface titration data, crystallographic data, and selenite surface saturation data. Two crystal face compositions were modeled due to the uncertainty related to the selenite bonding environment on goethite's capping face(s). The two face model (2FM) was comprised of the (101) and (210) crystal faces, while the three face model (3FM) utilized the (101), (001), and (210) faces. The 2FM assumes that selenite binds to all crystal faces as a double corner bidentate complex. The 3FM is based on spectroscopic evidence suggesting that selenite binds as an edge sharing complex on goethite's capping faces.

Both approaches predicted adsorption edges and isotherms in single and bi-solute Cd^{2+}/Pb^{2+} systems, but inclusion of a metal-selenite ternary complex was required to describe Cd^{+2}/SeO_3^{-2} and Pb^{+2}/SeO_3^{2} adsorption data. EXAFS experiments will be conducted in the upcoming year to confirm the presence of these metal-selenite complexes.

CD-MUSIC was also used to describe inorganic Hg(II) adsorption onto goethite. Data from Barrow and Cox (1992) and Bonnissel-Gissinger et al. (1999) were analyzed to capture the impacts of pH, ionic strength, carbonate, and chloride on the retention of Hg(II). The model successfully fit experimental data from systems containing Hg(II), CO_3^{-2}, and Cl^- through incorporation of the (≡FeOH)-Hg-(≡FeO) bidentate complex and the ≡FeO-HgCl monodentate ternary complex identified in published spectroscopic studies.

Predicting Fracture Porosity Evolution In Sandstone

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Funding: $300,000

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 the fully coupled diagenetic-geomechanical model.

FY 2012 HIGHLIGHTS

We documented basin scale fracture opening histories (Fall et al., 2012) and completed diagenetic modeling and laboratory experiments that show how mechanical properties evolve with progressive diagenesis. Fracture diagenesis' role in modifying rock permeability was explored via uncoupled geomechanical, fluid flow, and cement precipitation simulations. We developed a new that predicts fracture size scaling based on fracture cohesion. We documented vertical and lateral growth of a single large opening-mode fracture (length ~meter) and demonstrated that reconstructing fracture array histories is feasible. A technique developed to improve accuracy of open-fracture spacing estimations successfully predicted open-fracture spacing in horizontal cores and in outcrop examples. Laboratory tests and modeling highlighted how fracture growth and diagenesis can influence cohesion of pre-existing fractures in the presence of fractures created by hydraulic fracture treatments. We documented and explained the systematic mechanical properties differences existing in sandstone sequences, and showed how this is a byproduct of diagenesis and how this can influence fracture growth. We demonstrated the profound influence of sandstone composition, on mechanical properties and on fracture systems.

We successfully incorporated effects of diagenetic processes in our geomechanical model (Olson et al., 2009; 2010) but more sophisticated approaches are needed to take advantage of our understanding of diagenetic phenomena in fractures and host rocks. We developed code that predicts the extent of fracture bridging by quartz cement by accounting for euhedral/non euhedral nucleation surfaces, crystal size, temperature, and fracture opening rate and are experimenting with a new approach to predict bulk elastic properties through geologic time as well as permeability based on coupled sandstone diagenetic and rock physics models. We are extending the geomechanical code to incorporate diagenesis as well as a new poroelastic model that considers fluid flow effects, and we conducted core and outcrop based studies to test the model. Published results can be found on the project web site http://www.jsg.utexas.edu/sdi/.

Fault-Related CO_2 Degassing, Geothermics, and Fluid Flow in Southern California Basins: Physiochemical Evidence and Modeling

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Funding:	$124,000

PROGRAM SCOPE

This is a collaborative study with Prof. James R. Boles (UCSB) to quantify basin-scale fluid flow, submarine gas migration, and diagenetic effects within deforming faults in a transpressional setting that is seismically active. We have mainly targeted well known and active faults and young (Tertiary age) petroleum fields in southern California for study. Faults include the Refugio Fault in the Transverse Ranges, the South Ellwood Fault in the Santa Barbara basin, and the Newport-Inglewood Fault Zone in the Los Angeles basin. Several types of subsurface data (geophysical well logs, formation properties, pore-fluid pressures, and chemistry) are being studied to characterize the hydrogeologic history and geochemical signatures of fluids in these basins. These data provide constraints for mathematical models that are being developed to simulate with high-performance computing the likely fluid pressures, flow patterns and rates, subsurface temperature, and geochemistry associated with large fault systems.

FY 2012 HIGHLIGHTS

We have continued to refine a new computational model (TUFTS-FV) to study large-scale processes affecting multiphase fluid migration, including the effects of relative permeability, capillarity, and fluid saturation that affect hydrocarbon mobility within faulted sedimentary basins. A primary goal here is to understand the possible hydrogeologic conditions that enabled the natural trapping (sequestration) of prolific volumes of hydrocarbons in actively deforming young basins such as the Santa Barbara and Los Angeles basins. By building the 2-D Tufts-FV multiphase numerical model, one graduate student has successfully modeled large-scale fluid flow for faulted profiles of the Los Angeles basin; a second student is developing a 3-D reactive flow code (RST3D) to model fault mineralization and effects on permeability; and a third student is using an earlier 2-D software code (CPFLOW-GL) to analyze tidal signals associated with deep faults. For the Los Angeles basin, our simulations show that hydrocarbon reservoirs that are today aligned with the Newport-Inglewood Fault Zone were formed by massive hydrocarbon flows from deeply buried source beds in the central synclinal region. This happened during post-Late Miocene time, during a relative rapid period of petroleum migration, when about 3 billion barrels of oil migrated along major faults. Fault permeability, fluid capillarity forces, juxtaposition of aquifers (reservoirs) and aquitards, source-rock saturation, and the rate of petroleum generation controlled the efficiency of natural petroleum migration over a period of ~250,000 years. We expect that this hydrogeological research will also contribute to an understanding of the subsurface behavior of injected anthropogenic greenhouse gases, but more fundamentally to a better understanding of the physiochemical behavior of fluids in the deep subsurface, and the effects of chemical reactions and poroelasticity on fault permeability and multiphase fluid dynamics.

Impact of Micro- to Meso-Scale Fractures on Sealing Behavior of Argillaceous Caprocks on Carbon Sequestration

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Funding:	$171,000

PROGRAM SCOPE

We investigate the nature of fracture propagation, and fluid flow from reservoir rocks into overlying shale/siltstone at geologic analogs for CO_2 storage and hydrocarbon reservoir-seal pairs. The basic physics of capillary pressure trapping by fine-grained deposits depends on the fine-scale to microscale capillary and wetting properties of the fluids and grains, and any large [> 1-mm wide] imperfection at an interface may initiate seal failure. We examine this process with an integrated field, experimental, subsurface borehole geophysics, and modeling approach. Fieldwork focuses on examining the nature of fracture transitions between the top of reservoir analogs and their contacts with sealing lithologes. Experimental work, performed in conjunction with co-workers at Sandia National Laboratories, examines the elastic rock strength of a variety of rock lithologies in order to determine the elastic rock properties at reservoir conditions. Subsurface borehole-geophysics uses the sonic response of the rocks and porosity character to determine their properties at depth, and geomechanical modeling using a finite-element method examines the stress state and rock parameters controls on fracture growth across interfaces.

FY 2012 HIGHLIGHTS

Field work at three sites reveals that structural discontinuities act as loci for upward fluid flow, creating zones of fluid flow from the reservoir and breaching the overlying seal. We observe mineralization within fault damage zones, including previously envisioned “low permeability” fault deformation bands that, when imaged with new methods, can be seen to have been preferential fluid pathways in the subsurface. Field observations are supported by petrographic analysis and elemental analysis, which support the observation of host-rock alteration, fracture mineralization, and migration of fluids in the subsurface (Fe^{2+}). Field work across several interfaces at different structural settings indicates the influence of small faults on upward flow, and examination of faults with ~ 100 m of throw indicate seal bypass into thick seals.

Experimental work on rock properties largely agrees with borehole geophysics, in which elastic moduli vary significantly over short distances as a function of cementation and rock composition. These results help explain the stepped open-fracture – sheared fracture character to discontinuities that cut the multilayered seal. Numerical models further explore this behavior, and we show that the degree of contact strength, and stress transmission into strong, stiff rocks, results in open-mode fractures that remain open as the package is deformed.

Dissolution Rates and Sorption/Catalytic Reactivity of Nanominerals and Nanomineral Aggregates

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

PROGRAM SCOPE

The overall goals of this project are to (1) investigate the effect of particle size, morphology and aggregation state on the kinetics of reductive dissolution of nanoparticulate hematite, (2) determine size, morphology and reactive sites of nanohematite and their aggregations, (3) determine catalytic activity of nanohematite by testing aqueous Mn(II) oxidation, and (4) investigate the reactivity of nanoparticulate iron sulfides.

FY 2012 HIGHLIGHTS

Hematite nanoparticles (two populations averaging 7 and 31 nm in size) were synthesized and characterized using powder-XRD, TEM and BET surface area measurements. The influence of size, morphology, and aggregation state on the reductive dissolution of these nanohematites with ascorbic acid was carefully investigated in detail. The surface area normalized by the initial rate of reductive dissolution in the case of the 7 nm hematite is about two times greater versus the 31 nm hematite, and the longer term rate is about 50% greater. High-resolution TEM (HRTEM) of individual crystals and aggregates revealed contrasting differences in the 7 nm and 31 nm hematite; the former being relatively free of internal and external defects and the latter displaying nanoscale steps on their surfaces. In addition, high-angle annular dark-field scanning transmission electron microscopy of the 7 nm hematite revealed nanochannels within the rhombohedra that serve as highly active sites for dissolution. Our findings are of fundamental importance to understanding how certain crystal morphologies, internal structures, defects, and reactive sites occur in nanocrystals formed from a poorly crystalline precursor, ferrihydrite in this case.

The catalytic activity of nanoparticulate hematite was also investigated by testing its capacity to oxidize aqueous Mn(II). The end product of Mn(II) oxidation under circumneutral, room temperature conditions was found to be a mixed valent manganese oxide identified as the mineral hausmannite (Mn_3O_4). The hausamannite crystals produced using the nanohematite catalysts, characterized by employing a suite of analytical techniques including HRTEM, electron energy loss spectroscopy mapping, nanometer-resolved selected area electron diffraction (SAED), and high-resolution scanning electron microscopy (SEM), are remarkably fine nanowires with dimensions of 7 to 12 nm wide by up to microns in length. We anticipate that the observed euhedral, pyramidal terminations of these nanowires are exceptionally reactive, and are currently testing this hypothesis.

Finally, the dissimilatory metal-reducing bacteria *Shewanella putrefaciens* strain CN32 was used to synthesize biogenic mackinawite ($Fe_{1+x}S$). The nanosized biogenic mackinawite was characterized using SEM, TEM, HRTEM, and BET surface area analysis and Mössbauer spectroscopy. Reactivity of the biogenic mineral was tested by its propensity to reduce aqueous uranium. X-ray absorption spectroscopy and HR-TEM analyses indicated the formation of nanoparticulate (c.a. 2.5 nm) uraninite UO_2 on the surface of the biogenic mackinawite.

Investigation of the Physical Basis for Biomineralization

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Funding:	$260,000

PROGRAM SCOPE

This project is directed at determining principles that govern interactions of simple protein analogs and key inorganic impurities with carbonate minerals to produce the resulting structures, polymorphs, and signatures. The long-term goal is to establish the physical basis for biomineralization in natural and engineered Earth systems.

FY 2012 HIGHLIGHTS

We made significant advances that have the potential to shift the rapidly growing field of non-classical mineralization. Multiple new research publications are in advanced preparation that uncover biomolecule controls on carbonate growth and show the thermodynamic versus kinetic nature of their effects on mineralization. We also made new insights into the controls of organic templates on $CaCO_3$ nucleation, nucleation pathways, roles of Mg and supersaturation in $CaCO_3$ formation toward dolomitic compositions, kink dynamics of steps on calcite, and microscopic controls on trace element and isotopic fractionation.

In a pair of new papers, we show theoretically the thermodynamic barrier to calcite homogeneous nucleation is prohibitive on laboratory timescales at solution conditions above the solubility limit of ACC due to the magnitude of the interfacial energy between calcite and aqueous solution. This explains recent reports that ACC forms before calcite. However, they erroneously assumed the reason for this behavior is the existence of a non-classical pathway involving highly stable pre-nucleation clusters. Such species are not needed and would favor formation of calcite over ACC. We then show experimentally that the introduction of self-assembled monolayers with acidic headgroups substantially lowers the interfacial energy, leading to direct formation of calcite with a dependence on solution conditions that is in accordance with classical theory. We also use molecular dynamics to explain structural and energetic sources of the distinct differences in nucleation control exerted by SAMS comprised of odd versus even chain length monomers, and synchrotron-based measurements to demonstrate that the ability of SAM monomers to reorient is crucial for controlling nucleation.

We also report direct observations of ACC nucleation, coalescence, and crystallization via in situ TEM, using a fluid cell holder and electrochemical fluid cell design that was developed with supplemental funding to this project. These are the first measurements of their kind on natural mineral systems. In addition, we have applied that method to the study of particle-mediated growth. This mechanism—as opposed to ion-by-ion attachment—is now recognized as a common phenomenon in a wide variety of natural and synthetic crystallization systems. Using isotopic labeling and mass spectroscopy, we also investigated calcium isotopic fractionation in ACC, calcite growth through an ion-by-ion process, and ACC that transformed to calcite while in contact with solution.

Interface Induced Carbonate Mineralization: A Fundamental Geochemical Process Relevant to Carbon Sequestration

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

PROGRAM SCOPE

This program aims to study the effect of dissolved catalysts (like hydrogen sulfide) on crystallization of dolomite and high-magnesium calcite. This involves investigating the roles of non-carbonate minerals and solution chemistry in controlling the nucleation of individual carbonate polymorphs and compositions through a synergistic effect of substrate surface electric properties and the epitaxial coordination of the guest-host minerals.

FY 2012 HIGHLIGHTS

We investigated the effect of hematite (001) surface on nucleation of calcite and Mg-bearing calcite. The results show that hematite (001) surface can enhance heterogeneous nucleation of calcite. The calcite (001) // (001) of hematite. Due to hexagonal lattice of calcite and hematite, no twin-like relationship was observed among the calcite crystals grown on (001) surfaces. However, the crystals in the calcite twin relationship were observed among the calcite crystals grown on (001) surface of muscovite and biotite (with pseudo-hexagonal symmetry). The amount of calcite crystals increases and the amount of aragonite decrease as the lattice mis-match between calcite and substrate crystal decrease (from biotite, muscovite to hematite).

Heterogeneous nucleation results indicate that tremolite (a Ca-Mg amphibole) {*hl*0} surfaces promote nucleation of calcite better than diopside's surfaces. The step-like (001) surface of the double chains in tremolite (very similar to that in biotite) may adsorb Ca on the A sites and promote nucleation of calcite and high-magnesium calcite crystals.

We studied dissolved hydrogen sulfide (as catalyst) on incorporation and growth of disordered dolomite and high-magnesium calcite. Hydrogen sulfide can be adsorbed on calcite and dolomite surfaces. The adsorbed hydrogen sulfide (binding to carbonate anions through hydrogen bond) will weaken the bonding strength between surface Mg and water molecules. The role of adsorbed hydrogen sulfide serving as catalysts can lower the dehydration energy barrier of surface Mg^{2+}-water complexes dramatically and can, therefore, enhance Mg^{2+} incorporation into the dolomite structure.

Ion Microprobe Analysis of Oxygen and Silicon Isotope Ratios in Diagenetic Cements

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Funding:	$263,000

PROGRAM SCOPE

This project is developing and applying new techniques for in situ stable isotope analysis using a CAMECA IMS-1280 ion microprobe. This involves modifications to the SIMS instrument, development of new standards and procedures, and studies of diagenesis in the Illinois basin and elsewhere. We are investigating applications of the new analytical technology to CO_2 sequestration, paleoclimate, fossil fuel reservoirs, and groundwater and hydrothermal systems. Specific goals include (1) develop procedures for stable isotope analysis at 1 to 10 micron-scale by ion microprobe; (2) measure oxygen isotope growth zoning in individual quartz-overgrowths at micron-scale; (3) determine genesis, timing, and geometry of porosity reducing cements in Mt. Simon sandstone reservoir/aquifer of the Wisconsin Arch and the Illinois Basin and compare to comparable sandstones elsewhere; and (4) determine the presence, genesis, timing, and geometry of porosity reducing cements in Eau Claire shale aquitard of the Wisconsin Arch and the Illinois Basin.

FY 2012 HIGHLIGHTS

Significant advances have been made in the analysis and interpretation of stable isotope compositions, zonation, and exchange. We have applied experience gained by microanalysis of syntaxial quartz overgrowths in the St. Peter sandstone to quartz cements in the Mount Simon sandstone and overlying Eau Claire shale. New results show that deeply buried Mt. Simon quartz overgrowths are zoned in $\delta^{18}O$ recording growth during burial and heating (Pollington et al. 2011). We have found similar zoned cements in the Eau Claire Fm (Hyodo et al. 2012); Ness Fm., North Sea; and Wilcox Fm, Texas (Harwood et al. 2012). DOE-sponsored regional partnerships, MGSC and MRCSP, have drilled an injection well and two observation wells for a mega-ton CO_2 sequestration experiment in Mount Simon sandstone at Decatur, Illinois. Our study will provide a basis for interpretation of cementation in the sandstone aquifer and confining mudstone aquitard of this system. Specific achievements include: (1) developed new improved UV imaging system for analysis of stable isotope ratios by IMS-1280; (2) made first measurements of δ18O in traverses of single quartz overgrowths in Eau Claire Fm; (3) discovered gradients up to 10‰/50μm within diagenetic quartz with consistently declining δ18O through time due to increasing burial, heating, and pressure solution; and (4) proposed new Paleozoic basin-evolution model for development of porosity occluding cements in Mt. Simon and Eau Claire formations of the Illinois basin.

Phase Transitions and Crystal Orientations in Marine Invertebrate Skeletons: Key Insights into Biomineral Formation Mechanisms and Function

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Students: 1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding: $225,000

PROGRAM SCOPE

Biominerals include bones, teeth, mollusk shells, and many others and are formed under direct control of organisms. We propose to do state-of-the-art microscopy and spectroscopy experiments to elucidate key biomineralization mechanisms that have long puzzled the geochemistry community. Specifically we will strive to elucidate the propagation of crystallinity through amorphous precursor phases, the intriguing space-filling process of biomineral nanoparticles, and the ordering of biomineral components at various length scales, both in terms of formation mechanisms and functional biomechanics.

FY 2012 HIGHLIGHTS

The most important discovery we have made in Fiscal Year 2012 was to elucidate the sequence in time of mineral phases, their energetics, and their localization in sea urchin spicules. Specifically we successfully followed the amorphous-to-crystalline transitions by imaging them directly with 20-nm resolution (Gong et al. PNAS 2012), using the spectromicroscopy methods we developed and the spectroscopic signatures we previously identified (Politi et al. PNAS 2008, Killian et al. JACS 2009, Radha et al. PNAS 2010). Significantly, we identified the possible function of the SM50 protein *in vitro*. SM50 is the most abundant protein in spicules and all other calcite biominerals produced by sea urchins. *In vitro*, this protein appears to stabilize the hydrated phase of amorphous calcium carbonate. In the last year of this grant, we will seek to identify the function of this protein *in vivo* in sea urchin spicules and teeth. This is a very ambitious task which, if successful, will provide the protein function for SM50. This will be only the 4th of all thousands of biomineral proteins for which a function is identified. [The previous ones are collagen in bone (Nature 2008), starmaker in zebrafish otoliths (Science 2003), and Pif in mollusk shell nacre (Science 2009).]

New Tracers of Gas Migration in the Continental Crust

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Funding: $130,000

PROGRAM SCOPE

The central goal of this proposal is to enhance understanding of gas distribution and migration in the continental crust, using new measurements of noble gases in whole rocks and minerals from continental drill cores, with an emphasis on helium, neon, argon, and their relationships to carbon and nitrogen. Existing noble gas data sets are dominated by measurements of gas and fluid phases from gas wells, ground waters, and hot springs. There are very few noble gas measurements from the solid continental crust itself, which means that this important reservoir is poorly characterized, as are gas migration rates. Understanding gas migration rates and mechanisms is fundamental to carbon sequestration, hazard assessment, and resource management. Due to systematic variability in physical properties, such as diffusion, solubility, and production rates (from natural radioactive decay), along with their inertness, the noble gases provide unique indices of gas migration. In particular, the radiogenic production ratios of 4He/21Ne and 4He/40Ar are excellent indicators of fractionation because their production rates are defined by crustal abundances of Th, U, and K, which are relatively well understood. We will perform measurement of helium, neon, and argon abundances and isotopic compositions in a suite of drill cores from the continental crust near the Texas Panhandle, with the goal of exploiting these key indicators to understand the history of gas migration in the region. The geological context of the area is well constrained, and the measurements will be combined with crustal petrology, geochemistry, and volatile inventories. The Texas Panhandle gas field is the southern limb of the giant Hugoton-Panhandle oil and gas field; it has high helium contents (up to ~ 2 %) and 3He/4He of 0.21 (± 0.03) Ra, slightly above "typical" crustal production 3He/4He values. The highest helium contents are found above the Panhandle/Wichita uplift, consisting of faulted Precambrian basement. Because the total amount of helium in the Panhandle gas field is relatively well known, crustal isotopic data and mass balance calculations should constrain the ultimate source rocks, and hence the migration paths. A key strategy will be to carry out measurements by crushing *in vacuo* to examine the gas released from fluid inclusions, followed by melting to release gas from the mineral/rock matrix. This simple procedure will determine the fraction held within fluid inclusions, potentially providing a direct measure of gas migration history of specific lithologies.

FY 2012 HIGHLIGHTS

The first step is to construct an ultra-high-vacuum line dedicated to the extraction of gases from continental rocks, allowing the measurements to proceed without hydrocarbon contamination of the mass spectrometers. The design of the extraction line began during this fiscal year, with particular consideration of compatibility with existing vacuum equipment in this laboratory. This project began in September 2012.

Fluid Chemistry, Surface Chemistry and Fracture Mechanics: An Investigation of the Connection at the Nanoscale

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Funding:	$89,000

A summary for this program was not available at press time.

DOE National Laboratories

Mineral-Fluid Interactions: Synchrotron Radiation Studies at the Advanced Photon Source

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Funding:	$600,000

PROGRAM SCOPE

This proposal seeks funding to continue the development of 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 include adsorption/desorption, growth/dissolution, and oxidation/reduction processes that play a critical role in controlling the bio-availability of nutrients and the sequestering or transport of toxins. The program strategy emphasizes direct molecular-scale observations of fundamental geochemical processes through in situ studies at mineral-fluid interfaces. This is achieved by taking advantage of the unique characteristics of the Advanced Photon Source (APS) at Argonne National Laboratory, including the unprecedented x-ray beam properties available at this 3rd generation synchrotron facility (e.g., beam brilliance, flux, and tunability). These properties allow fundamentally new types of in situ experiments of mineral-fluid interfaces to be performed, including the ability to visualize the interfacial structure at an interface 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 help to constrain the continued development of theory pertinent to mineral-fluid interface processes.

We continue to address these gaps in our understanding through a two-pronged approach. We will make experimental observations of elementary mineral-water interface processes in well-defined systems to test our understanding of fundamental processes with established experimental approaches and through direct comparison to theoretical results. Our emphasis will be on understanding the inter-relationships between structural, thermodynamic, and kinetic controls of interfacial processes related to ion adsorption and growth/dissolution processes at mineral-water interfaces. This will be obtained through observations that probe the temporal evolution of the interfacial structure and the relationship of these changes to spatial heterogeneities. The fundamental knowledge obtained from this proposed work will lead to a more robust understanding of the factors that control the transport of elements through the near-surface environment that is necessary for the development of robust predictive capabilities associated with the geological disposal of energy byproducts (e.g., carbon sequestration, nuclear repository).

FY 2012 HIGHLIGHTS

We have made new measurements of the calcite-water interface structure and the adsorption of monovalent cations at the muscovite–water interface. These results show that the previously reported structures for these systems are incomplete and provide a benchmark for ongoing studies where these results will be compared to the results of parallel computational studies.

Detection and Monitoring of Fluids, Faults and Coupled Processes in the Earth's Crust

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Students:	1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$1,475,000

PROGRAM SCOPE

Fluids are commonly injected into the Earth's crust for a variety of important industrial reasons, including sequestration of CO_2, geothermal energy generation, ground-water clean up, enhanced oil recovery. In these applications, it is desired to know where in the Earth the fluids go and what they do; e.g., are they inducing fracture or dissolving minerals and thus disrupting the flow barriers that are hoped to contain them in the subsurface? The goal of this research is to use changes in recorded geophysical signals (seismic and electromagnetic) as well as satellite measurements of surface deformation and recordings of seismicity to monitor where the injected fluids migrate and what they do. The specific objectives in this first phase of effort are to (1) understand and model how faults in the Earth become unstable during fluid injection and how they become more stable during chemical healing, (2) understand how geophysical rock properties of the subsurface change during fluid injection and through induced fracture, and (3) develop inversion procedures that exploit such forward models and allow measurements of deformation, acoustic emissions, and controlled-source geophysical signals to provide images of fluids and processes in the subsurface. A combination of laboratory experiments, theoretical modeling, and numerical modeling are used to address these objectives.

FY 2012 HIGHLIGHTS

On the rock properties and fracture mechanism front, a novel laboratory device was constructed that measures fracture stiffness over the range of seismic frequencies used in exploration work (10^{-1} to 10^{2} Hz). This device measured the seismic response as fractures were filled with different fluids, the fluid pressure was changed, and the fractures were healed by chemical precipitation of minerals. A new method was developed that allows calcite to rapidly precipitate in both fractures and granular media. In order to better detect the presence of large fractures in the Earth, a new mode of acoustic waves in fluid-filled fractures, called a *Kraukalis wave*, was studied that allows a fracture to resonate and thus be detected at certain frequencies. For the first time, a Kraukalis wave was measured in the laboratory and its properties were compared favorably to theoretical predictions. Also, for non-cemented granular media, which are very sensitive to changes in fluid pressure, the role of loose grains in the pack was theoretically modeled in an attempt to explain the large amounts of seismic attenuation observed in such materials. Lastly, two studies are nearing completion on fluid-induced seismicity that use data from a special project at the Geysers geothermal field in northern California. The source mechanisms of earthquakes near an injection well indicate that both shearing and a change in volume are involved in these events. An extended crack model was developed that explains these two processes and provides estimates of crack dimension, orientation, and amount of slip.

On the monitoring front, a theory was developed that tracks coupled deformation and flow in a medium with properties that depend upon fluid pressure. 15 snapshots of surface deformation, obtained from satellite-based Interferometric Synthetic Aperture Radar data, were inverted using the developed theory to infer pressure disturbance propagation times and flow paths within a producing gas field. Finally, work continued on the joint inversion of seismic and EM data. Successful inversion codes were developed that assume the spatial variations of electrical conductivity are linked to the variations of seismic velocity. Cross-plots of the inverted velocity-resistivity attributes can be used for subsurface lithofacies discrimination, which is important to our ability to model flow.

Integrated Isotope Studies of Geochemical Processes

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Funding:	$825,000

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) the behavior of isotopes and trace elements in large-scale hydro-geochemical systems. Advanced 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 new geochronological techniques as well as methods for characterizing transport 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 Sr, Mg incorporation during mineral precipitation, isotopic fractionation associated with aqueous diffusion of cations, anions and dissolved gases, 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 sulfur and Fe isotopic fractionation during abiotic sulfide reduction, kinetic isotopic effects on soil carbonate isotopes, and modeling of isotopic effects due to fracture flow and inhomogeneous permeability in fluid-rock systems.

FY 2012 HIGHLIGHTS

We developed a new ion-by-ion growth model for calcite that predicts the variable Ca isotopic fractionation associated with non-equilibrium growth from oversaturated solutions. This model uses known or estimated energy and structural parameters and available experimental data to provide a self-consistent description of the kinetics of crystal growth and Ca isotopic fractionation as a function of growth rate. A key result is that Ca isotopic fractionation, as well as growth rate, should depend on the Ca:CO3 ratio of the solution as well as on solution saturation state. Experiments with biogenic calcite indicate that, where amorphous calcium carbonate is a precursor of calcite or aragonite, Ca isotopic fractionation is different from conditions where calcite precipitates directly. To evaluate whether models for calcite can be extended to higher temperature, we made measurements of natural Ca-bearing minerals (epidote and calcite) in high temperature geothermal systems. Epidote at 350C and calcite at 150C show evidence of kinetic isotopic fractionation effects similar to those of calcite at 20C. Measurements from natural systems suggest that the presence of clays and organic material can modify calcite dissolution and affect isotopic and trace element partitioning.

Interconnections between Dynamic Processes that Control the Formation, Evolution, and Reactivity of Environmental Interfaces

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Students:	2 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$1,750,000

PROGRAM SCOPE

A wide range of important geochemical phenomena, including mineral nucleation, aggregation, dissolution and growth, as well as surface adsorption and redox reactions, involve dynamic processes that occur at natural environmental interfaces. These important geochemical reactions critically affect the chemistry of soils and surface waters. Many of these dynamic processes are intimately interconnected; a reaction such as mineral growth comprises a wide range of molecular-scale changes in the coordination, speciation, and electronic structure of atoms at the interface. This research project uses experimental and simulation methods to obtain detailed knowledge of the chemistry of important mineral-water interfaces; the processes through which these interfaces are formed, transformed, or lost; and the impacts of these processes on the chemistry of the environment.

FY 2012 HIGHLIGHTS

(1) The early stage development of iron oxyhydroxyl polymers in solution mimicking AMD formation has been investigated in sulfate and nitrate solutions using time-resolved SAXS, UV-vis spectroscopy, quick EXAFS, in-situ XRD, Mössbauer spectroscopy of quick-frozen solutions, and cryo TEM methodologies.

(2) We are evaluating a model that we developed for adsorbed water films, based on the Derjaguin-Landau-Verwey-Overbeek analysis. This model allows the thickness of films of water on mineral surfaces to be predicted based on the matric potential, van der Waals interactions, solution chemistry, and interfacial (mineral-water and gas-water) charge.

(3) We carried out MD simulations to test the ability of existing interatomic potential models to predict x-ray reflectivity data on the adsorption of potassium at mica-water interfaces.

(4) We have developed two complementary approaches to modeling ion diffusion through clays. The first makes use of a Donnan equilibrium approach in which a mean electrostatic potential is defined for the electrical double layer to balance the fixed negative charge of the clays. The second approach involves the use of the Nernst-Planck and Poisson-Boltzmann equation (termed the P-N-P method).

(5) We reveal that the interface between a bulk fluid and a silicate surface consists of an altered amorphous Si-rich surface layer (ASSL). By considering ASSL as a separate phase that can control silicate dissolution rates, we show that the extrapolation of laboratory-based rates at conditions relevant to the field can be lowered by several orders of magnitude, potentially reconciling field and laboratory chemical weathering rates.

(6) We perform the first direct measurements of the electron hopping rate in three phases of iron oxide and oxyhydroxide.

(7) Mercury(II)-reacted FeS samples were analyzed using Hg L_{III}-edge extended X-ray absorption fine structure (EXAFS) spectroscopy at 10 K in order to elucidate the speciation of Hg after equilibration with FeS.

Inv. of the Physical Basis for Biomineralization III

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Students:	2 Postdoctoral Fellow(s), 3 Graduate(s), 2 Undergraduate(s)
Funding:	$200,000

PROGRAM SCOPE

This project is directed at determining principles that govern interactions of simple protein analogs and key inorganic impurities with carbonate minerals to produce the resulting structures, polymorphs, and signatures. The long-term goal is to establish the physical basis for biomineralization in natural and engineered Earth systems.

FY 2012 HIGHLIGHTS

We made significant advances that have the potential to shift the rapidly growing field of non-classical mineralization. Multiple new research publications that uncover biomolecule controls on carbonate growth and show the thermodynamic versus kinetic nature of their effects on mineralization are in advanced preparation. We also made new insights into the controls of organic templates on $CaCO_3$ nucleation, nucleation pathways, roles of Mg and supersaturation in $CaCO_3$ formation toward dolomitic compositions, kink dynamics of steps on calcite, and microscopic controls on trace element and isotopic fractionation.

In a pair of new papers, we show, theoretically, the thermodynamic barrier to calcite homogeneous nucleation is prohibitive on laboratory timescales at solution conditions above the solubility limit of ACC due to the magnitude of the interfacial energy between calcite and aqueous solution. This explains recent reports that ACC forms before calcite. However, they erroneously assumed the reason for this behavior is the existence of a non-classical pathway involving highly stable pre-nucleation clusters. Such species are not needed and would favor formation of calcite over ACC. We then show, experimentally, that the introduction of self-assembled monolayers with acidic headgroups substantially lowers the interfacial energy, leading to direct formation of calcite with a dependence on solution conditions that is in accordance with classical theory. We also use molecular dynamics to explain structural and energetic sources of the distinct differences in nucleation control exerted by SAMS comprised of odd versus even chain length monomers, and synchrotron-based measurements to demonstrate that the ability of SAM monomers to reorient is crucial for controlling nucleation.

We also report direct observations of ACC nucleation, coalescence, and crystallization via in situ TEM, using a fluid cell holder and electrochemical fluid cell design that was developed with supplemental funding to this project. These are the first measurements of their kind on natural mineral systems. In addition, we have applied that method to the study of particle-mediated growth. This mechanism—as opposed to ion-by-ion attachment—is now recognized as a common phenomenon in a wide variety of natural and synthetic crystallization systems. Using isotopic labeling and mass spectroscopy, we also investigated calcium isotopic fractionation in ACC, calcite growth through an ion-by-ion process, and ACC that transformed to calcite while in contact with solution.

Geochemical Imaging with Nano/SIMS

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Funding:	$100,000

PROGRAM SCOPE

The NanoSIMS is a recently developed secondary ion mass spectrometer with lateral spatial resolution as good as 50 nm. Coupled with its high transmission, the instrument has the potential to address a number of geochemical problems that were heretofore intractable, essentially taking trace element and isotopic analysis to a spatial scale approaching that of transmission electron microscopy. The performance and applicability are only now being developed for geochemical applications. This project will contribute to the development of geochemical imaging in three applications to naturally- and experimentally-produced materials that are related by the need for high-resolution imaging. Current efforts are focused on the partitioning of moderately siderophile elements between core-forming metallic liquids and silicate melts. The work combines more conventional measurements using piston cylinder and mulit-anvil apparatus with measurements in the laser heated diamond anvil cell.

FY 2012 HIGHLIGHTS

Metal-silicate partitioning experiments at high pressure (35-74 GPa) and temperatures (3000-4400⍰⍰) demonstrate that depletions of slightly (V, Cr) and moderately (Ni, Co) siderophile elements can be produced by core formation under more oxidizing conditions than previously proposed. Enhanced solubility of oxygen in the metal perturbs the activity coefficients of siderophile elements, precluding extrapolation of previous results. We propose that the Earth accreted from materials as oxidized as carbonaceous or ordinary chondrites. Transfer of oxygen from the mantle to the core provides a mechanism to reduce the initial redox to that of the present-day mantle, reconciling the observed mantle concentrations of Co, V and geophysical constraints on light elements in the core.

Kinetic Isotope Fractionation

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Funding:	$50,000

PROGRAM SCOPE

The primary objective of the proposed research is to explore and quantify isotopic fractionations (i.e., isotopic fingerprints) associated with mass transport processes within and between phases, one of which is in most cases a liquid—either water or a silicate melt. The Lawrence Livermore National Laboratory effort on this project involves measuring the isotope fractionation of chemically diffusing species using the GV IsoProbe, the Nu Plasma multi-collector ICP-MS, and the Cameca NanoSIMS. In FY 2008 we proposed to make new basalt-rhyolite diffusion couples similar to those used in Richter et al. (2003) to measure the kinetic isotope fractionation of Mg and Fe associated with the chemical diffusion of these elements between molten basalt and rhyolite. We also proposed to expand studies of isotopic fractionation driven by thermal gradients (i.e., Soret diffusion).

FY 2012 HIGHLIGHTS

We analyzed silicate melt diffusion couples for U and Pb isotopics and concentration. The U and Pb concentration measurements were made by Q-ICP-MS, the U isotopics were analyzed on both IsoProbe and Nu Plasma MC-ICPMS, and the Pb isotopics were analyzed on the Nu Plasma only. The U concentration results show a very slight gradient. Uranium concentration measurements by Isotope Dilution Mass Spectrometry (IDMS) will achieve much higher precision/accuracy. The Pb concentration data do not show a gradient along the couple. A Pb spike is required for more precise/accurate Pb concentration measurements by IDMS.

Quantification of Mineral Precipitation Kinetics Using Solution Chemistry and NMR Spectroscopy

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Funding:	$225,000

PROGRAM SCOPE

This project is designed to investigate the processes that affect the formation and precipitation of minerals in aqueous geochemical environments. We combine water chemistry with NMR spectroscopic methods to elucidate these reaction pathways. Characterizing how minerals form from solution in aqueous environmental systems is a basic need in a variety of fields from geothermal energy to waste remediation. A fundamental need is to understand what role prior existing surfaces play in the formation of accessory mineral phases.

FY 2012 HIGHLIGHTS

It has been largely assumed that the end product of the alteration reactions with calcium silica hydrates is amorphous silica based largely on mass balance calculations. We are employing micro-tomography and NMR measurements to identify the major mineral constituent of the amorphous layer as an amorphous aluminosilicate in cements that have been reacted in CO_2 rich fluids. Preliminary findings suggest that the amorphous layer is similar to the zeolite phase mordenite, which contains mobile structural waters. The reactions involving Al are important given the influence that even small amounts of Al can have on the precipitation and dissolution of silicate minerals, but have been largely overlooked in cement reactions. The ^{27}Al NMR data show that the alteration induces a change from $Al^{[6]}$ sulfate minerals to $Al^{[4]}$ silicate minerals. This finding is counter to prior assumptions that Al should partition into $Al^{[6]}$-oxides/hydroxides. This data suggests that previously “invisible” Al has dissolved from the Fe-rich Ca-aluminate phases and partitions into the amorphous aluminosilicates.

Uranium-Series Environmental Transport and Geochronology Studies

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Funding:	$250,000

PROGRAM SCOPE

The goal of this project is to evaluate in situ uranium-series analytical techniques with applications for geochemistry and geochronology. We aim to measure, model, and understand U-series isotopic distributions over a range of spatial and temporal scales (micron to kilometer and years to millennia) while contributing to the continued development of micro analysis methods. We are examining new femtosecond laser ablation techniques coupled with a new state-of-the-art MC-ICP-MS, calibrated by well calibrated characterized geologic standards. Technique evaluation is achieved by the study of U-series transport/retention in fractures in proximity to natural uranium deposits, U-series and actinide transport/retention in soils, and the U-series geochronology of corals. Through this work we aim to further understand the geochemistry of mineral-water interactions and assessment of radioactive waste repositories, along with other hydrologic and geochemical processes.

FY 2012 HIGHLIGHTS

We have successfully characterized a number of newly available glass standards for U-series isotopes by thermal ionization mass spectrometry. These standards are being used by us to calibrate our laser ablation methodologies. The results of these analyses have been presented at the AGU fall meeting in San Francisco. We have also recently completed the installation of a Nu Plasma II MC-ICPMS. We have continued to work on developing methods for U-series analysis on our femtosecond laser system, identifying and addressing long term stability issues. Suitable U-rich fracture samples have been identified and preparation begun for in situ and bulk measurements (by laser ablation, MC-ICP-MS, and MC-TIMS). These samples represent the first tests of our new methodologies. The new methods, new understanding, and newly trained researchers that result from this work also actively contribute to interests of other agencies such as environmental monitoring and threat reduction.

A New Probe for Understanding Rock Elasticity - Time of Flight Modulation

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Funding:	$250,000

PROGRAM SCOPE

The focus of our work is the application and development of advanced elastic nonlinear methods for probing the elasticity of material, based on the dynamic acousto-elasticity (DAE) nonlinear probe, in which a material is cyclically stressed dynamically at low frequency while simultaneous measures of wave speed are made. The results will have applications in monitoring thermally-induced mechanical damage in nuclear repositories, probing borehole integrity, as well as geotechnical applications, including monitoring infrastructure, groundwater reservoirs; and broad application to earthquakes and strong ground motion. Moreover, the work involves major advances in the basic research in the domain of elastic nonlinearity. The research initiates development of a model that provides predictive capability relating elastic nonlinear response to mechanical damage intensity.

FY 2012 HIGHLIGHTS

We have made progress in both laboratory studies and in small-scale field studies applying DAE. A primary focus has been to quantify the DAE method, to understand experimental limitations, and to develop more sophisticated data processing and interpretation procedures. A second focus has been to characterize a suite of different rocks and rock types to explore elastic behavior differences that may be compositionally and/or mechanically based. In regards to this second study area, we observe characteristic elastic nonlinear behaviors for different rock types. We infer that these differences reflect differences in mechanical damage state—the primary contribution to the nonlinearity at fixed pressure, humidity, and temperature conditions. Thus granite exhibits different elastic behavior than sandstone and limestone for instance. This work was published in the *Journal of Geophysical Research* and a second manuscript is under review in *Geophysical Research Letters*. We also conducted a field study applying DAE applying a 60-ton vibrational source known as *T-Rex* operated by the University of Texas at Austin. Detectors were placed in several boreholes to probe the effects of the vibration-induced nonlinearity in soil layers. This work holds promise as one approach for site characterization, and a manuscript is in preparation. Our work on quantification of the method has produced an elegant analysis procedure, and we now have a firm grasp on experimental problems that may lead to interpretation error. A manuscript describing this work is nearly ready for submittal. Our work has led to a significant number of patents that are granted or in progress (>10), for characterizing and imaging reservoirs.

Summer of Applied Geophysical Experience (SAGE)

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Sr. Investigator(s):	
Students:	0 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$40,000

PROGRAM SCOPE

The Summer of Applied Geophysical Experience (SAGE) is a unique program designed to introduce geophysics students to geophysical exploration and research. Its purpose is to enhance a student's knowledge by going beyond a standard classroom-based geophysics curriculum, and to encourage qualified students in related fields to consider careers in geophysics. The course focuses the student's preparation and experience on geological problems of research and practical interest. Students combine geophysical data, acquired using a variety of techniques, with knowledge of the geological setting to derive integrated subsurface interpretations. Processing and modeling of geophysical data are PC and workstation-based, using state-of-the-art software. Modern field equipment and vehicles are provided by various academic institutions and industrial affiliates. The SAGE faculty consists of active, dedicated, and experienced researchers. Students are predominantly upper division or graduate students in geophysics or related disciplines from a variety of U.S. and foreign institutions, and professionals from various earth science fields. SAGE has operated in the Rio Grande rift in New Mexico since 1983.

FY 2012 HIGHLIGHTS

Objectives of SAGE 2012 included (1) providing hands-on training and research experiences in basic and applied geophysics for 25-30 graduate and undergraduate students, (2) conducting innovative research on a variety of important Earth science problems, and (3) introducing students to a range of career opportunities in geophysics. Research results are expected to make significant contributions in a number of national security areas, such as the development of new energy sources, nuclear and non-nuclear waste disposal, environmental remediation, groundwater resources, and carbon sequestration. Results will also impact basic research related to the structure and tectonics of continental extension. SAGE faculty members are from LANL, several universities, the U. S. Geological Survey, and various companies. SAGE 2012 conducted research on two related topics. In the northern Albuquerque basin of the Rio Grande rift, several geophysical surveys were undertaken to examine basin depth and the role of connected and overlapping faults in accommodating deformation. This study furthers understanding of how individual faults link into deformation zones that form a boundary of a major, active continental rift. The second project was undertaken to identify and characterize mainly subsurface, man-made structures at an archaeological site, one of the largest pre-Columbian cities of the American Southwest.

The study also served as a proxy for evaluation of tools and techniques applicable to smaller-scale environmental-restoration and waste-disposal sites. Geophysical techniques included seismic reflection and refraction, gravity, time-domain electromagnetics and controlled-source (active) magnetotellurics, magnetics, and ground-penetrating radar; and integration with existing industry seismic data, aeromagnetic data, surface geological mapping, and borehole information.

Molecular Mechanisms of Interfacial Reactivity in Near Surface and Extreme Geochemical Environments

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Funding:	$70,000

PROGRAM SCOPE

This project aims to develop predictive understanding of the geochemical processes involved in mineral transformations in wet supercritical CO_2. CO_2 storage safety and long-term caprock integrity play important roles in the site selection and operation of large-scale carbon sequestration projects. This project, which is part of a geoscience research program led by Andrew Felmy at Pacific Northwest National Laboratory, is concerned with the interactions of supercritical CO_2 with swelling clays that comprise major constituents of caprocks. Concerns are that the caprock formation overlying buoyant CO_2 plumes at injection sites can become permeable to CO_2 through diffusion and wetting processes, as well as crack formation through volume changes in the clay components. In order to evaluate the extents and rates of these seal-quality-degrading processes, we study clay mineral - CO_2 interactions at the nanoscale by combination of excess sorption and neutron diffraction techniques. Emphasis is put on the impacts of hydration level, interlayer cation identity, and temperature and pressure.

FY 2012 HIGHLIGHTS

We have completed a detailed study of the interactions of supercritical CO_2 with sodium montmorillonite clay in its sub-monolayer hydration state. Such dehydrated states are likely in natural rocks exposed to dry supercritical CO_2. Experimental results show that supercritical CO_2 does enter the clay interlayers in limited quantities and can partially substitute for hydration water, leading to swelling of sub-monolayer hydrated montmorillonite. The structure of the CO_2-substituted clay is stable over extended ranges of pressure and temperature, indicating that the sealing performance of the clay components will not be affected by changes in these parameters if the clay maintains its hydration state.

Structure and Dynamics of Earth Materials, Interfaces and Reactions

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Chialvo, Ariel, Oak Ridge National Laboratory
Stack, Andrew, Oak Ridge National Laboratory
Anovitz, Larry, Oak Ridge National Laboratory
Students: 4 Postdoctoral Fellow(s), 3 Graduate(s), 0 Undergraduate(s)
Funding: $1,850,000

PROGRAM SCOPE

The overarching goal of this project is to obtain a fundamental, atomic- to macro-scale understanding of the structure and dynamics of complex natural fluids and minerals, and their interactions from ambient conditions to elevated temperatures and pressures. Achieving this goal will allow us to quantitatively predict the factors driving the evolution of fluid-rock interactions, resulting from the interplay of fluid properties, mineral heterogeneity and stability, local equilibrium, interfacial phenomena, and kinetics of chemical reactions. We address three key interrelated challenge areas relevant to mineral-fluid interactions that are encountered at conditions ranging from the Earth's surface to deep within the crust and mantle: (1) *How can we accurately predict the effects of environmental conditions on the structural, energetic and dynamic properties of complex fluids and minerals encountered in natural and engineered geological environments?* (2) *How do altered fluid and mineral properties emergent at fluid/solid interfaces influence phase transformations and mass transfer along and across the interface?* (3) *How do we couple fundamental atomistic understanding of bulk and interfacial structures and dynamics in complex heterogeneous systems with transport and reactivity over geologically-relevant time and length scales?* A scientifically diverse, multi-institutional team utilizes novel experimental and analytical techniques in concert with state-of-the-art theory, modeling and simulation approaches to address these issues applied across the full range of environmental conditions encountered at the Earth's surface and in the crust.

FY 2012 HIGHLIGHTS

Neutron reflectometry was employed to probe the effect of solution pH on the structure of phospholipid bilayers that form spontaneously on mineral surfaces and may have played a role in the evolution of early life on Earth. Small angle neutron scattering and backscattered electron imaging were employed to characterize the changes in porosity and permeability of a sandstone aquifer as a result of groundwater flow during burial and geological deformation. Fluid-cell atomic force microscopy (AFM) was employed to develop a model for the effect of strontium (a common constituent of nuclear waste streams) on the growth and dissolution rates of the common mineral calcite ($CaCO_3$). We demonstrated accurate prediction of the growth and dissolution rates of ionically-bonded minerals like calcite and barite ($BaSO_4$) by coupling rare event theories with molecular dynamics simulations. For the covalently-bonded mineral quartz (SiO_2), we have integrated ab initio and classical molecular dynamics simulations with synchrotron X-ray reflectivity to elucidate the role of dissolved salts on growth and dissolution rates. Finally, we have developed a unique experimental approach (vibrating tube densimetry) to directly measure the effect of nanoscale confinement on the density of pore-filling fluids under realistic geology temperature and pressure conditions.

Molecular Mechanisms of Interfacial Reactivity in Near Surface and Extreme Geochemical Environments

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Ilton, Eugene, Pacific Northwest National Laboratory
Rosso, Kevin, Pacific Northwest National Laboratory
Zachara, John, Pacific Northwest National Laboratory
Chaka, Anne, Pacific Northwest National Laboratory
Students: 4 Postdoctoral Fellow(s), 4 Graduate(s), 1 Undergraduate(s)
Funding: $1,500,000

PROGRAM SCOPE

The Basic Energy Sciences (BES) Geosciences Research Program managed at PNNL is designed to advance our fundamental understanding of molecular processes to determine the mechanisms that control interfacial reactivity in near surface to extreme geochemical environments. Specific aspects of the research program are focused on (1) unraveling the impact of electron conduction/transfer reactions on the dynamics of mineral interfacial reactions and the changes induced in mineral surface chemistry, (2) determining the molecular/microscopic mechanisms responsible for mineral/water film nucleation and growth in geochemical environments including non-aqueous fluids, and (3) the development and application of 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 as well as more complex rock-water interactions, which is critical for accurately predicting the consequences of geologic disposal of the byproducts of energy production activities.

FY 2012 HIGHLIGHTS

In FY 2012, the research focused on electron transfer reactions of iron oxides and the development of new electronic structure methods for treating transition metals. Specifically, hematite and goethite redox interaction with aqueous Fe(II) were investigated in detail in order to assess various free energy components needed for a thermodynamic model that can be used to predict the rate and extent of involvement of the bulk conduction mechanism. Studies on the incorporation of U(VI) in the structure of hematite have also shown that the U coordination environment is uranate-octahedral, and that U(V) was the dominant oxidation state consistent with theory. Laboratory studies with both synthetic abiotic and biotic ferrihydrite showed the influence of surface speciation promoted by groundwater inorganic cations (Ca^{2+}, Mg^{2+}, and Mn^{2+}), anions (H_4SiO_4, H_3PO_4, and HCO_3^-), and organic matter on the electron transfer rates of $Fe^{2+}_{(aq)}$; reduced flavins FMN, RBF, and FAD; and multi-heme cytochrome complexes. New tools for electronic structure calculations are also being developed that include faster, more scalable methods for density functional (DFT) calculations of band structures and 1st principle dynamics; more efficient hybrid DFT implementations; and electronic structure methods which more accurately treat electron correlation in materials with highly localized d and f valance orbitals (e.g., transition metal oxides).

Molecular Mechanisms of Interfacial Reactivity in Near Surface and Extreme Geochemical Environments

Institution: Pacific Northwest National Laboratory
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Dixon, David, Alabama, University of
Students: 2 Postdoctoral Fellow(s), 3 Graduate(s), 2 Undergraduate(s)
Funding: $632,000

PROGRAM SCOPE

This project is conducting a comprehensive experimental and theoretical investigation of the role of interfacial water and CO_2 on the energies, mechanisms, and rates of reactivity of a series of orthosilicate and phyllosilicate minerals in contact with supercritical-CO_2 ($scCO_2$) containing variable H_2O. The microscopic and molecular mechanisms for carbonation reactions, as well as the distribution of H_2O between $scCO_2$ and mineral surfaces, will be followed using molecular simulations and surface spectroscopy as a function of T, P, mineral composition and structure, and H_2O activity. The theoretical studies will be coupled with high-resolution spectroscopic measurements [e.g., IR/FTIR, NMR, TEM, and Helium Ion Microscope (HIM)] to investigate the formation and structure of water layers at mineral surfaces and in the interlayer region of phyllosilicates, and to identify potential interfacial carbonate and silicate species. The macroscopic reactivity of the orthosilicates and the changes in interlayer water structure and reactivity of the phyllosilicates will be determined experimentally using high pressure cells. The speciation and reactivity trends will be interpreted using a newly developed thermodynamic model, capable of extrapolation to extremely high ionic strengths present in highly water-depleted fluids. The proposed research will provide new insights into mineral transformations under extreme conditions and help establish a basis for assessing the effectiveness of CO_2 sequestration in geologic disposal sites.

FY 2012 HIGHLIGHTS

This project was initiated at the end of FY 2009. Research to date has established that water plays a catalytic role in orthosilicate reactivity and water can be effectively recycled in low water content $scCO_2$ solutions by the formation of anhydrous divalent metal carbonates. Water recycling during orthosilicate reactivity can greatly increase the extent of metal carbonation. This research has been instrumental in unraveling long-standing challenges in carbonate chemistry related to this nucleation and growth of anhydrous mineral phases such as magnesite. The structure of water on the orthosilicate surface is also being probed by IR/FTIR spectroscopy and by using molecular dynamics simulation. The reactivity of phyllosilicates is also being examined by NMR spectroscopy and by using a new in situ XRD unit that allows us to probe interfacial binding of both CO_2 and water during reaction.

Geochemistry on Interfaces: From Surfaces to Interlayers to Clusters

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Students:	1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$750,000

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 2012 HIGHLIGHTS

We have made progress in force field development for species on the edges of clays using hydrated oxide models. Vibrational frequencies from normal mode analysis of the classical models are matched to the results of DFT calculations yielding classical parameters for bond stretch and bond-angle bend. We continued using MD simulation and inelastic neutron scattering to study water vibrational behavior in smectite minerals. We have collected INS spectra of hydrated and dehydrated montmorillonite and beidellite at LANSCE for samples exchanged with various alkali and alkaline earth cations.

We continued to study the interfaces between goethite (FeOOH) and aqueous NaCl, $MgCl_2$, or $BaCl_2$ solutions using classical MD simulations. Water layers near the (100) surface are strongly structured, while those above the (101) surface are more diffuse. The water dipole orientation dominates the surface charge profile into bulk solution even in the presence of salt. Sufficient study was completed to determine that oxyanions cannot be simulated successfully with a simple-point-charge water model. Ab initio MD simulations to determine the pKa for the monodentate $FeOH_2$ group on (101) were completed (prediction of 7.0).

Various iron-oxo clusters have been synthesized. Structural characterization of the clusters requires multi-dentate ligation (e.g., acetates, alkoxides) for isolation in crystalline form. Additionally, it is challenging to re-dissolve these species intact, once isolated. The crystalline forms reveal ferric cluster geometries and fragments found also in early d^0 transition-metal oxide clusters; the former are capped by organic ligands and the latter by 'yl'-oxo ligands. By careful hydrolysis of Fe^{III} solutions followed by mass-spectral analysis, we have identified nucleation species, the most common of which contain sixteen Fe-centered polyhedra.

Non-Darcian Flow, Imaging, and Coupled Constitutive Behavior of Heterogeneous Deforming Porous Media

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Students:	0 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding:	$600,000

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 2012 HIGHLIGHTS

We have developed novel methods for characterization of 3D pores in gas shales and other mudstones relevant as caprocks for carbon sequestration or hydrocarbon seals. Through work with academic colleagues on small angle neutron scattering, traditional mercury porosimetry combined with FIB/SEM imaging has led us to develop a canonical view of mudstone pore types, including macro (> 1 micron), micro (< 1 micron and > 10 nm), and nano-pore types (< 10 nm). Pore topology (arrangement and connectivity of these pore types) depends both on inherited depositional characteristics as well as burial history, and extent and type of organic material, and controls whether fluid flux through mudstones is Darcian or not. Comparison of pore-scale simulations and core-scale measurements suggest that single phase Darcian fluid flow at permeabilities of 1-10 nanodarcies is controlled by connected networks of pores 20 nm and larger in size, and non-darcian type flow laws are better suited for many mudstones that lack such a connected microporosity. In some mudstones, nanopores (below FIB/SEM resolution) contribute up to half of the total porosity and at least 80% of total surface area, and in effect yield a partially-drained effective stress behavior. Micropore-lining phases, which influence membrane efficiency and wettability, can be distinctly different from bulk phase mineralogy estimated from x-ray methods. Micropillar compression and typical core-scale axisymmetric compression tests show scale-dependence of compressive strength and Young's modulus, and are examining scale dependence of anisotropy.

Experiments imaged by CT-scanning are guiding efforts to best represent pore topologies in percolation models in porous media with mixed wettability. Medial axis software has been developed to convert CT images from the experiments to pore network models. Pore network models based on several medial axis methods are compared. Results include pore network statistics, computational efficiency, and direct comparison to 3DMA results. Percolation software to include these effects is under development. Preliminary code models capillary flow in an unstructured pore network model (output from medial axis software). The code accounts for capillary pressure, hydrostatic pressure, and mixed wet media. The code includes criteria to vacate pores, check for trapped clusters, and to select the most invadable finger. An experimental method tracking changes in pore distribution and percolation under axial and radial stress conditions is under development.

A rigorous thermomechanical constitutive framework for deforming high porosity geomaterials is being developed and an ultrasonic monitoring system unique to Sandia is being adapted to provide experimental validation. Sub-tasks that are being investigated include a testing method that tracks effective stress response through elastic loading into plastic yielding, a series of experiments designed to test applicability of nonassociative plasticity and nonisotropic hardening, and a testing suite that rigorously examines localization predictions of the constitutive theory. Ultrasonic imaging methods for tracking p- and s-wave velocity and dynamic moduli evolution during hydrostatic, constant shear, and other non-traditional loading paths are being developed. These are critical to separating bulk engineering strain into elastic and plastic parts, and will allow, e.g., a novel tracking of isotropic and anisotropic Biot's parameters during plastic straining.

Heavy Element Chemistry

Institutions Receiving Grants

Probing the Actinide-Ligand Binding and the Electronic Structure of Gaseous Actinide Molecules and Clusters Using Anion Photoelectron Spectroscopy

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

PROGRAM SCOPE

The broad scope of this program is to better understand actinide chemistry using new spectroscopic techniques and to provide accurate spectroscopic data for the validation of new theoretical methods aimed at actinide chemistry. This program contains three thrust areas: (1) probing ligand-uranyl (UO_2^{2+}) interactions in gaseous anionic complexes in the form of $[UO_2L_x]^{n-}$ produced by electrospray ionization, (2) probing the electronic structure and bonding of inorganic and organometallic compounds of actinides in the gas phase using electrospray and anion photoelectron spectroscopy, and (3) probing the metal-metal bonding and size-dependent electronic structures in U_x^- and $U_xO_y^-$ clusters as a function of size and composition.

FY 2012 HIGHLIGHTS

Uranyl tetrafluoride ($UO_2F_4^{2-}$) and its solvation complexes by one and two water or acetonitrile molecules are investigated by photoelectron spectroscopy and *ab initio* calculations. The isolated $UO_2F_4^{2-}$ dianion is found to be electronically stable with an adiabatic electron binding energy of 1.10 ± 0.05 eV. The photoelectron spectra of the solvated complexes by H_2O and CH_3CN are observed to be similar to those of the bare $UO_2F_4^{2-}$ dianion, suggesting that the solvent molecules are coordinated to the outer sphere of $UO_2F_4^{2-}$ with relatively weak interactions between the solvent molecules and the dianion core. Both DFT and CCSD(T) calculations are performed on $UO_2F_4^{2-}$ and its solvated species to understand the electronic structure of the dianion core and solute-solvent interactions.

The UF_5^- and UF_6^- anions are produced and studied. An extensive vibrational progression is observed in the photoelectron spectra of UF_5^-, indicating significant geometry changes between the anion and the neutral ground state. An accurate electron affinity is obtained for UF_5. Relativistic quantum calculations using density functional and *ab initio* theories are performed on UF_5^- and UF_6^- and their neutrals. The ground states of UF_5^- and UF_5 are found to have C_{4v} symmetry, but with a large U−F bond length change. The ground state of UF_5^- is a triplet state ($^3B_2$) with the two 5f electrons occupying a $5f_z3$-based $8a_1$ highest occupied molecular orbital (HOMO) and the $5f_{xyz}$-based $2b_2$ HOMO-1 orbital. The detachment cross section from the $5f_{xyz}$ orbital is observed to be extremely small, and the detachment transition from the $2b_2$ orbital is more than ten times weaker than that from the $8a_1$ orbital at the photon energies available. The UF_6^- anion is found to be octahedral, similar to neutral UF_6 with the extra electron occupying the $5f_{xyz}$-based a_{2u} orbital. Surprisingly, no photoelectron spectrum could be observed for UF_6^- due to the extremely low detachment cross section from the $5f_{xyz}$-based HOMO of UF_6^-.

Fundamental Chemistry of Actinide Complexes Containing An-N, An-O, and An-S Bonds

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Funding:	$125,000

PROGRAM SCOPE

The objective of this research is to expand knowledge of actinide chemistry to provide fundamental information on actinide metal-ligand bonds that may be useful in the development of advanced nuclear energy cycles. In addition, this research provides training of graduate students in the science of the f orbital metals, the lanthanides and actinides. Recent studies of the reaction chemistry of An−H and An−C bonds (An = U, Th) demonstrated that surprising new structures and reactivity patterns were available from well-established classes of actinide complexes, some of which have been known for decades. The goal of this project was to attempt to similarly expand the limits with other donor atoms and especially nitrogen.

FY 2012 HIGHLIGHTS

New U-N chemistry was discovered by examining the radical chemistry of well-defined organoactinide complexes to obtain more information about the radical reactivity of actinide-element bonds. Examination of NO as a radical reagent provided the first nitrosyl $(NO)^{1-}$ complex of any f element, lanthanide or actinide. Since the $(NO)^{1-}$ ligand is a pseudo-halide and the f elements form many types of complexes with halides, it was surprising that this ligand had never been found with these metals. The new complex, $(C_5Me_4H)_3U(NO)$, has an unusual structure not seen before in NO complexes of any metal. Moreover, it proved to be a new example of actinide-element multiple bonding with significant U=N double bond character. The complex also displayed unusual temperature independent magnetism.

Efforts to make more soluble complexes dense in U and N for conversion to UN led to exploration of the $(\eta^5\text{-}C_5Me_4SiMe_3)$ ligand. Surprisingly, a dialkyl metallocene complex of this ligand formed $(\eta^5\text{-}C_5Me_4SiMe_2CH_2\text{-}\kappa C)_2U$, a complex that has two tethered U-C bonds. This was used to make the first uranium metallocenes with tethered U-N bonds. Since tethering can change the entropic aspects of reactions, this may allow new U-N based transformations to be identified. U-N chemistry was also investigated with the tetramethylpyrrole ligand. The metallocene complex, $(C_5Me_5)_2U(NC_4Me_4)$, was synthesized along with lanthanide analogs that allowed Ln vs U comparisons. These complexes were found to crystallize with many structural variations, showing the flexibility of these metals in making bonding arrangements.

Uranium Complexes for the C-H Activation of Hydrocarbons

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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

Uranium complexes containing ferrocene-based ligands provide an interesting platform to study the electronic interaction between iron and uranium. Understanding the electronic communication between iron and uranium in ferrocene complexes allows the development of new catalytic systems and reactivity. The work proposed will result in expanding the fundamental knowledge about metal-metal interactions and in establishing new reactivity for uranium complexes. This research also trains the next generation of actinide scientists by providing graduate, undergraduate, and post-graduate education on the chemistry of the f elements.

FY 2012 HIGHLIGHTS

The objective of this research project is to study the reactivity of uranium complexes supported by ferrocene-based ligands. During the past year, we characterized mixed-valent bis-ferrocene uranium complexes. Mixed-valent bis-ferrocene complexes have been studied intensively in order to understand the dependence of electronic coupling between the two iron centers on the linker connecting them. In the bis-ferrocene systems of interest to us, the f orbitals of uranium allow strong electronic coupling between the iron centers. The participation of f orbitals in covalent bonding is still a hotly debated topic; by designing a system in which uranium interacts directly with a transition metal, we have created a unique class of compounds to use as a basis to address this question.

Exploring the Redox and Oxo Substitution Chemistry of the Uranyl Ion: Expanding our Understanding of Uranyl Reactivity and Behavior

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Students:	0 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding:	$150,000

PROGRAM SCOPE

Understanding the bonding and reactivity of uranyl (UO_2^{2+}) is critical for understanding its 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, this project aims 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. These studies could have industrial significance, with potential applications in the processing of nuclear fuel.

Additional goals of this project are to synthesize and study new uranyl analogues, specifically the chalcogen analogues of uranyl, $[E{=}U{=}E]^{2+}$ (E = S, Se, 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.

FY 2012 HIGHLIGHTS

We have recently synthesized and structurally characterized the first terminal selenide and telluride complexes of uranium, namely, $[Ph_3PMe][U(E)(NR_2)_3]$ (E = Se, Te). They can be accessed by oxidation of $U(CH_2{=}PPh_3)(NR_2)_3$ (R = $SiMe_3$) with elemental selenium or tellurium, respectively. Interestingly, the U=Se and U=Te bond lengths are the shortest yet observed for these elements, indicating substantial multiple-bond character in the U=E interaction. Mechanistic studies suggest that the ylide ligand in the starting material, $U(CH_2{=}PPh_3)(NR_2)_3$, plays an important role in U=E bond formation by limiting the availability of U(III) in solution. This observation may lead to new synthetic methods for generating uranium-ligand multiple bonds. This work was recently published in the *Journal of the American Chemical Society*.

Selective Recognition of Heavy Elements by Protein-Based Reagents

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Students:	1 Postdoctoral Fellow(s), 1 Graduate(s), 1 Undergraduate(s)
Funding:	$165,000

PROGRAM SCOPE

The objective of this project is to engineer protein-based reagents that can selectively bind heavy elements in aqueous solutions. Our long-term goal is to design and evolve proteins that can bind individual actinide ions tightly and selectively. In the past year, we have made two breakthroughs that will be described below.

FY 2012 HIGHLIGHTS

(1) Uranyl-selective binding proteins based on a Protein Data Bank screen. We computationally screened all published protein crystal structures in the Protein Data Bank for uranyl-selective binding sites. Out of 4,000 hits, we selected 10 hits from the top 100, synthesized these genes, expressed the proteins, and tested uranyl binding. Four proteins were shown to bind uranyl at nM affinities. We performed further rational protein engineering on one of the uranyl-binding proteins. After several rounds of design, test, structural characterization, mutagenesis, and redesign, we obtained a robust uranyl-binding protein with a K_d of 6.1 femtomolar (fM) and > 10,000-fold selectivity over other metal ions including calcium(II). We named this protein SUP for super uranyl-binding protein.

Since uranyl is soluble in water, the concentration in seawater is surprisingly high at 3.2 mg/ton of seawater (13 nM). The ocean contains 1,000 times more uranium than land, offering an enormous resource that, unlike land resources, may be tapped at minimal environmental cost. To effectively sequester uranyl from seawater requires the development of uranyl-binding ligands with femtomolar or higher affinity to uranyl and > 1 million-fold selectivity over calcium(II) and other abundant metal ions present in ocean. *No existing small molecule or protein-based ligands can achieve this daunting task*. We showed that when immobilized on a polymer support or displayed on a cell surface, SUP can repeatedly and efficiently sequester uranyl from seawater. Up to 60% of uranyl in synthetic seawater can be effectively sequestered.

(2) Lanthanide and actinide-sensing bacteria. The survival and growth of *E. coli* and *Salmonella* species require iron as one of the essential nutrients. They have evolved a PmrA/PmrB two-component system to sense the presence of iron(III) in the environment and to regulate the response of the bacteria. PmrB is a transmembrane sensor/kinase that uses a 30-amino acid iron-binding motif to sense iron(III) outside of the bacterial membrane. Upon iron(III) binding, the signal is transduced across the membrane and the cytoplasmic domain of PmbB phosphorylates PmrA, the DNA-binding regulatory protein of the system. Unmodified PmrA cannot bind DNA, while the phosphorylated PmrA binds specific promoters in the bacterial genome to activate the expression of genes involved in the response. We have replaced the iron(III)-binding motif in PmrB with a lanthanide/actinide-binding tag.

Spectroscopic and Theoretical Studies of Prototypical Actinide Compounds

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Funding:	$130,000

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 ThF/ThF$^+$, UF/UF$^+$, and ThS/ThS$^+$.

FY 2012 HIGHLIGHTS

Spectra for ThF and ThF+ showed that the bonding and electronic structures of these molecules are closely similar to the properties exhibited by the isoelectronic species HfF and HfF$^+$. ThF$^+$ is a molecule of interest for studies of the electron electric dipole moment (eEDM, a CP violation effect). Prior to our work, there were no spectroscopic data for this ion. Our measurements show that ThF$^+$ is the most promising ion for investigation of the eEDM. Theoretical prediction of the low-lying states of ThF$^+$ proved to be particularly challenging, such that the data are of value for the development of improved basis sets for Thorium. The UF$^+$ ion is isoelectronic with UO, and we have carried out spectral surveys that encompass more than 50 low-lying vibronic states. Manifolds of electronic states that arise from the metal-centered $5f^37s$ and $5f^27s^2$ configurations have been identified. The results validate ligand field theory models for both UO and UF^+. In addition, our highest level electronic structure calculations for UF^+ were in respectable agreement with the experimental results. Data for neutral UF indicated that a previous matrix isolation spectrum attributed to this molecule should be re-assigned. Previous theoretical calculations for ThS were inconclusive regarding the nature of the electronic ground state. Gas phase spectra show that it is a closed-shell molecule ($^1\Sigma^+$) with a low-lying triplet state ($^3\Delta_1$) at an energy of 0.265 eV. Hence, the state ordering is the same as that of ThO. Photoionization of ThS revealed states that correlate with the $Th^{3+}(7s)S^{2-}$ and $Th^{3+}(6d)S^{2-}$ configurations. Term energies, vibrational constants, and the ionization energy have been determined.

Control of Hydrothermal UO_2^{n+} Systems: A Solution Phase Approach to New Solid State Materials

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Funding:	$100,000

PROGRAM SCOPE

The goal of this program is to explore solution phase approaches to the formation of novel uranyl bearing hybrid materials. These include the use of in situ ligand syntheses (ISLS) and supramolecular assembly of uranyl tetrahalide species. ISLS reactions continue to be developed as offering unique routes to novel architectures. In a typical synthesis of a uranyl hybrid material, $[UO_2]^{2+}$ cations are assembled through multitopic organic linker molecules and then forced to crystallize. The linkers are often straight-forward, commercially available carboxylates or phosphonates. ISLS generated species, on the other hand, are formed from reactive organic precursors under hydrothermal conditions. As a consequence, hydrolysis or decomposition products then serve as the linker species and often result in topologies not otherwise obtainable via direct assembly.

Supramolecular assembly efforts also target novel hybrid materials, yet from the approach of using non-covalent interactions to crystallize (for example) uranyl tetrahalide anions and related species. The use of H-bonding and halogen-halogen interactions to link inorganic polyhedra through cationic organic species with appropriate supramolecular synthons continues to evolve and produce a range of novel materials. Supramolecular assembly is entirely undeveloped in actinide chemistry and as such, we are establishing a series of rules or guiding principles for predictable and rational assembly of aqueous phase species. Moreover, the resulting compounds provide unique forums for spectroscopic study of isolated uranyl centers.

FY 2012 HIGHLIGHTS

Efforts during 2012 have resulted in four publications that highlight the approaches outlined above.

(1) M. B. Andrews and C. L. Cahill (2012) "Uranyl Hybrid Material Derived from In Situ Ligand Synthesis: Formation, Structure, and an Unusual Phase Transformation." *Angew. Chem. Int. Ed.*, 51(27), 6631-6634. DOI: 10.1002/anie.201202402.

(2) M. B. Andrews and C. L. Cahill (2012) "Utilizing hydrogen bonds and halogen-halogen interactions in the design of uranyl hybrid materials." *Dalton Trans.*, 41(14), 3911-3914. DOI: 10.1039/c2dt11985d.

(3) G. Liu, N. P. Deifel, C. L. Cahill, V. V. Zhurov, and A. A. Pinkerton (2012) "Charge Transfer Vibronic Transitions in Uranyl Tetrachloride Compounds." *J. Phys. Chem. A*, 116(2), 855-864. DOI: 10.1021/jp210046j.

(4) M. B. Andrews and C. L. Cahill (2012) "Uranyl Hybrid Material Derived from In Situ Ligand Synthesis: Formation, Structure, and an Unusual Phase Transformation." *Angew. Chem. Int. Ed.*, 51(27), 6631-6634. DOI: 10.1002/anie.201202402.

Actinide Incorporation and Radiation Effects in Layered Structures

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Funding:	$100,000

PROGRAM SCOPE

The objective of this study is to derive comprehensive kinetic models for the reduction of oxidized actinyl complexes on semiconducting oxide and sulfide surfaces, and the oxidation (or oxidative dissolution) of the surfaces themselves. A focus of this study is the role of the surface atomic and electronic structure in mediating interactions between co-adsorbates (e.g., oxidized complexes, inorganic and organic reductants, and background electrolytes in solution) on the surface. The strength of our approach is a unique combination of molecular simulations (quantum mechanical to account for charge and electron spin transfer); electrochemical methods; batch experiments with subsequent XPS, SEM, and TEM analysis; and surface probe techniques to describe surface-mediated redox mechanisms and to resolve individual rate-determining steps. Molecular simulations will predict possible activated states that can occur between co-adsorbates on the surface and give insight into the reaction mechanism itself, especially steps that may be rate limiting, such as spin transfer, ligand reorganization, bond breaking, or mass transport (to name a few). Microelectrode techniques that have not traditionally been applied to study environmental reactions will be used to rapidly evaluate surface-specific mechanisms and kinetics in multivariable space. Finally, electrochemical surface probe microscopy will be employed to visualize these surface redox processes in-situ.

RESEARCH GOALS

(1) Resolve kinetics of adsorption/reduction into sub-processes such as bulk diffusion in bulk solution, surface diffusion, stripping of hydration sphere, adsorption, and overcoming activated states due to incompatible orbital symmetries or spin transitions.

(2) Use a combination of quantum-mechanical calculations; electrochemical powder micro-electrode measurements; batch experiments with subsequent TEM, XPS, and ICP-MS analysis; and electrochemical AFM measurements to resolve overall reaction path and mechanism and evaluate which of the sub-processes controls kinetics as function of environmental parameters (pH, pe,T, ionic strength, etc.), solution chemistry, and catalytic mineral surface.

(3) Use the information gained to help develop a strategy for optimizing reaction conditions for given applications, such as actinyl immobilization in permeable reactive barriers or geologic barriers near nuclear waste repositories, and to understand the geochemical behavior of actinyl phases in the environment.

Multiconfigurational Quantum Chemical Study of Actinide and Lanthanide Containing Systems

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Students:	2 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$301,000

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 will involve 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. In collaboration with Dr. Gibson, we will also study the interaction of actinides with biomolecules, which may occur in the case of contamination by actinides.

(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; study the bimetallic reductive elimination between the dimeric U^{4+} dihydride $[(C_5Me_5)_2UH_2]_2$ and the dimeric U^{3+} monohydride $[(C_5Me_5)_2UH]_2$; and study single molecule magnets (SMMs) containing from two to six uranium atoms, with bridging arene group.

(3) The ground and excited states of actinide and lanthanide ions in solution: We will investigate actinide chemistry in solution, which is related to the separation, transport in the environment, and safety of nuclear waste disposal. We will study some of the systems investigated experimentally by Dr. Lynda Soderholm by employing a combined quantum mechanical and classical simulation approach. We will begin by investigating the structure of the homoleptic Th(IV) aqua ion $[Th(H_2O)_{10}]$. Using the same approach, we will then study the solution coordination environment of pentavalent and hexavalent Np ions. The last challenge will be to study also electronically excited states of ions in solution. We would like to simulate the electronic spectrum of Gd^{3+} and Cm^{3+} in water to aid in the optical detection of these ions, by taking into account the thermodynamic accessibility of the excited states and the reactivity of these compounds in the excited states.

In order to address these problems, we will employ state-of-the-art quantum chemical methods, including multireference methods, which are currently developed in our group, and simulation techniques based on force fields derived from first principles.

American Chemical Society's Summer School in Nuclear and Radiochemistry

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Students:	0 Postdoctoral Fellow(s), 4 Graduate(s), 24 Undergraduate(s)
Funding:	$288,000

PROGRAM SCOPE

Numerous reports over the last decade have raised concerns regarding the number of well-trained nuclear scientists available to address critical national needs in defense, energy, medical sciences, and fundamental research. The Nuclear and Radiochemistry Summer Schools were initiated to help address the need for an undergraduate pipeline in response to the decline in educational opportunities in the field and concomitant lack of student exposure to the field. The objective of the Summer School in Nuclear and Radiochemistry is to increase the number of outstanding physical science and engineering undergraduate students introduced to nuclear chemistry and radiochemistry.

The Summer Schools are intensive, six-week courses in fundamental principles of nuclear and radiochemistry, held at San Jose State University (SJSU) and at Brookhaven National Laboratory (BNL). Each site serves 12 students annually. Participating students are introduced to course materials and activities that they would not be exposed to at their home institutions, broadening their perspective on this vital field of chemistry. As a result of their participation, approximately 20% of the 577 graduates of past summer schools chose to pursue advanced degrees in nuclear science disciplines and have subsequently found career positions in research or applied nuclear science fields, including positions with the US Department of Energy National Laboratories.

FY 2012 HIGHLIGHTS

The 2012 Summer Schools received 110 applications. The 24 participants (14 male/10 female) came from small colleges (14) and research universities (10) and had an average GPA of 3.8. Lecture topics included natural radioactivity, modes of decay, decay rates, interactions of radiation with matter, nuclear reactions, nuclear structure, fission and fusion, accelerators and reactors, nuclear power, actinide chemistry, nuclear waste management, environmental radiochemistry, and fundamentals of nuclear medicine. The laboratory exercises covered a sequence of experiments that illustrate fundamentals of radiation detectors and data acquisition systems, nuclear-based methods of chemical quantitative analysis, and preparation and purification of a radiopharmaceutical compound. At BNL, students toured the Relativistic Heavy Ion Collider, the Brookhaven LINAC Isotope Producer, the National Synchrotron Light Source, and the Indian Point Nuclear Power Plant. At SJSU, students visited the National Ignition Facility, the Seaborg Institute, the Center for Accelerator Mass Spectrometry, and the Synchrotron Light Source and Linear Accelerator Center at Stanford University.

Preorganized and Immobilized Ligands for Metal Ion Separations

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Funding:	$145,000

PROGRAM SCOPE

This project seeks to discover structural and electronic factors that impact selective recognition and binding of metal ions with donor group-decorated organic architectures. The primary targets for metal ion recognition are actinide and lanthanide fission product ions as they appear in aqueous nuclear material process solutions found in the DOE complex. The project is fundamental in nature, yet it is grounded on specific practical objectives. The experimental program employs a process of iterative, computationally assisted ligand design that suggests ligand synthesis targets, subsequent *f*-element ion coordination chemistry, spectroscopy and structure determination for isolated complexes, followed by liquid-liquid extraction analysis. Those ligand families that demonstrate novel, structure-function performance stimulate subsequent cycles of ligand design/synthesis activity.

FY 2012 HIGHLIGHTS

During the preceding year and currently, the specific major attention has been and continues to be in studies of geometric and electronic modifications of CMPO, NOPO, and NOPOPO fragments and their marriage to form hybrid architectures that encapsulate *f*-block ions. Several of these systems demonstrate useful metal ion partitioning. Additional ligand modifications are under development that should permit attachment of the active binding site to a polymer support or inclusion of the ligand fragment in a reversible polar/non-polar solvent system. Such materials would reduce or eliminate the impact of organic solvents in large scale nuclear separations.

Experimentally Characterizing the Electronic Structures of f-Electron Systems Using Advanced High Resolution Fourier Transform Microwave Spectroscopie

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Funding:	$115,000

PROGRAM SCOPE

We aim to provide (1) data that directly addresses the fundamental roles of actinide valence electrons in chemical bonding, and (2) prototypical data for the heavy element computational chemistry community. These goals will be achieved through the first pure rotational spectroscopic measurements on prototypical systems at ultra-high resolution. These systems encompass low oxidation state uranium and thorium compounds, including but not limited to UX and ThX, X = F, Cl, Br, I, UY, ThY, Y = O, S, and other simple U- and Th-containing compounds. Our primary experimental tools involve time-domain rotational spectroscopy achieving line widths and resolutions of a few kHz.

FY 2012 HIGHLIGHTS

We purchased two new laser ablation target rods, thorium and uranium, and made safe the locations in which the experiments are to be performed. This operation followed the relocation of equipment from Texas to New York. We performed preliminary broadband searches for pure rotational spectra from uranium monochloride, followed by uranium monosulfide and, most recently, thorium monosulfide. These preliminary searches have, to date, been unsuccessful. To counter this set back, we have spent several weeks working on the sensitivity of the instrumentation, making considerable improvements. Using the known spectra of tin monosulfide, we have improved signal-to-noise ratios from approximately 50:1, to approximately 300:1. Experiments suggest that this can be further improved by a factor of 2. Should this still be insufficient for signal detection, we have the option of switching to a cavity instrument with a further order of magnitude signal-to-noise improvement. Numerous, successful, quantum chemical calculations have been performed on the target molecules, and these will further aid in the spectral searches.

Computational Studies of NMR and EPR Parameters for Molecules Containing d- and f-Elements

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Funding:	$280,000

PROGRAM SCOPE

The main goal of this project is the theoretical prediction and analysis of paramagnetic NMR (pNMR) chemical shifts in actinide complexes encountered in nuclear waste and in ground water (e.g., carbonate complexes), and in lanthanide models of nuclear waste forms. There is an urgent need for theoretical support in this area. Another project goal is the prediction and analysis of electron paramagnetic resonance (EPR) parameters for lanthanide and actinide compounds, in order to establish a firm relationship between observable EPR parameters and the electronic structure of the complex. New methods are also tested on well characterized transition metal complexes and model systems with f-elements.

In this project, we develop and apply relativistic theoretical methods for the computation of ligand pNMR chemical shifts and EPR parameters for molecules containing heavy f- and d-elements. To a first approximation, the pNMR chemical shift is given by a combination of the 'regular' NMR shielding with EPR parameters; and, therefore the computations and related method developments are mutually beneficial. As part of the project, new density functional theory (DFT) approaches are tested for a more accurate theoretical treatment of electron correlation. Further, multi-reference theoretical methods are applied and developed in order to be able to treat complicated electron structures with unpaired electrons. New methods are mainly implemented in the DOE-supported open-source quantum chemistry program NWChem.

FY 2012 HIGHLIGHTS

(1) Detailed analysis of EPR hyperfine coupling by means of scalar relativistic DFT computations explain the origin of sign and magnitude of ligand pNMR shifts in metallocene complexes [J. Chem. Theor. Comput. 8, 598-609 (2012)].

(2) Analysis of hyperfine coupling in metal acac complexes shows a strong sensitivity on the DFT delocalization error [Inorg. Chem., 51, 8340-8351 (2102)] (which can be eliminated with procedures that we devised recently [J. Phys. Chem. Lett., 3, 576-581 (2012)]).

(3) A new class of formally exact two-component (X2C) Hamiltonians and arbitrary-order Douglas-Kroll-Hess (DKH) has been implemented in NWChem and tested with calculations of nuclear electric field gradients [J. Chem. Theor. Comput. (2012) in press (DOI: 10.1021/ct300623j)].

(4) The PI wrote an invited 'Perspective' article on relativistic quantum chemistry in which the aforementioned relativistic methods and applications of the PI's developments are discussed broadly [J. Chem. Phys., 136, 150902-15 (2012)].

(5) New methods for DFT calculations of EPR g-factors from spin-orbit relativistic DFT calculations were implemented and tested on a diverse set of molecules, including actinide fluoride complexes [submitted for publication in J. Chem. Theor. Comput.].

(6) A number of other studies by the PI have benefited from synergy due to method developments in the NWChem package that were needed for this project. These developments have been acknowledged accordingly in related publications [Chem. Eur. J., 18, 12803-12813 (2012), Phys. Rev. Lett. (2012) in press].

Fundamental Chemistry of Technetium-99 Incorporated Into Metal Oxide, Phosphate and Sulfide Materials: Towards Stabilization of Low Valent Technetium

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Funding: $260,000

PROGRAM SCOPE

The overall goal of the program is to investigate the fundamental chemistry of technetium-99 in inorganic matrices such as metal oxides, metal sulfides, and phosphates from size scales ranging from molecules to solid-state materials. Technetium-99, a major by-product of uranium-235 fission, presents challenges in separations and containment strategies due to its complex redox chemistry. As the pertechnetate ion is highly mobile, this consortium focused on investigation of low valent Tc compounds and materials. The scope of the program is multi-fold: (1) to identify new strategies for synthesizing low valent Tc dimers and polymers, (2) to identify new molecules to elucidate the reduction of pertechnetate by iron sulfides and their interferences, and (3) to identify features of molecular metal oxides that promote stabilization of low valent Tc and to demonstrate that these metal oxides can facilitate reduction of pertechnetate and covalent incorporation of the reduced Tc.

FY 2012 HIGHLIGHTS

The highlights of the research from this consortium are multi-fold. (1) Five new binary halide solid-state materials were identified by x-ray crystallography. These are important because they provide understanding of metal-metal bonding that may be very important for development of metal-based solid-state wasteforms. These provide starting materials for synthesis of other analogs. Another highlight is the development of hydrothermal synthesis strategies for low valent technetium materials; this is another step in understanding structure and coordination chemistry of low valent solid-state Technetium materials. (2) Unsaturated organic acids were found to be interferences in the reduction of pertechnetate by sulfides. Studies of the interaction of pertechnetate with multiple minerals and soil mimics are being completed to understand immobilization and stability of the reduced Tc-mineral. (3) New strategies allowed the syntheses of new technetium metal oxides. A combination of experiment (electrochemistry, x-ray absorption spectroscopy, multinuclear NMR) and DFT calculations resulted in an understanding of the features of the metal oxide defects that contribute to the stability the low valent Tc incorporated into the defects. This study highlights the impact of the electronic and steric features of metal oxide defects on the chemical properties and stabilities of incorporated low valent Tc. Moreover, these metal oxides are electron transfer agents that can be photoactivated to reduce pertechnetate. The low valent technetium is incorporated into the defect. All together, the features of metal oxides and other inorganic materials bear on the reduction of pertechnetate and the stabilization of the reduced technetium.

Polymer-Supported Complexants: Metal Ion Selectivity and the Variables of Rational Design

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Funding:	$145,000

PROGRAM SCOPE

The selective complexation of targeted metal ions from multi-component solutions has numerous applications that are critical to the DOE mission including groundwater and surface water remediation, recovery of metals from low-grade ores, mining and industrial wastewater treatment, intra-lanthanide separations, platinum group metals separations, and lanthanide/actinide separations. The focus in this research is on ligands immobilized onto polymer supports as either beads or membranes due to their ease of application to numerous separations. In designing separations, the current paradigm is one of empirical design wherein new ligands are prepared based on ligands that have worked in similar separations. This research proposes a paradigm shift: to design ligands based on an understanding of the variables of greatest influence on the selective interaction of metal ions to ligands. The research thus studies variations in the parameters affecting the ligand (polarizability and conformational rigidity), metal (polarizability, ionic radius, hydration, and geometry), and polymer (conformational rigidity and polarity). Metal ion affinities are quantified; and, as the variables of greatest importance are defined, those variables can be used in the *a priori* design of polymer-supported complexants.

FY 2012 HIGHLIGHTS

The polarizability of the phosphate ester ligand is affected by the presence of surrounding –OH groups, and this leads to enhanced metal ion affinities. This was determined through the synthesis of polymer-bound cyclodextrin (CD) that was phosphorylated with diethyl phosphate ligands. Earlier studies had shown that phosphorylated pentaerythritol had the highest metal ion affinities while the current results found that the phosphorylated CD (pCD) had an even greater affinity for the uranyl ion. For example, the percent complexed from solutions of 1.0 N HNO_3, HCl, and H_2SO_4 containing 10^{-4} M uranyl ions were 94.7%, 90.5%, and 93.6%, respectively, for pCD and 68.6%, 52.1%, and 40.1% for the phosphorylated pentaerythritol.

Hydrogen bonding within a urea ligand was found to give much enhanced lanthanide ion affinities: the urea ligand bound to cross-linked poly(vinylbenzyl chloride) had a very high affinity for lanthanide ions from acidic solutions, especially from HCl greater than 4 M.

A new synthesis strategy was developed for the immobilization of ligands because it was considered preferable to have a common starting point from which functionalization reactions can occur to study an array of ligands. This was accomplished by determining that polymer-bound pentaerythritol can be converted into a more reactive product by bromination, and the more reactive brominated pentaerythritol led to a series of ligands. For example, the reactivity of the $-CH_2Br$ moiety was shown by its subsequent reaction with diethylamine. The product had a far greater affinity for the uranyl ion from acidic solutions than the control derived from the reaction of diethylamine and poly(vinylbenzyl chloride): the control sorbed 1% of the uranyl ion from a 1.0 N HNO_3 solution while the product from the current research sorbed 85%.

New Synthetic Methods and Structure - Property Relationships in Neptunium, Plutonium, and Americum Borates

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Funding:	$135,000

A summary for this program was not available at press time.

Topological Structural Relationships, Cation-Cation Interactions, and Properties of U(VI), Np(V), Th(IV) Compounds

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Funding:	$135,000

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.

Accurate Theoretical Approaches for Studying the Chemistry of Actinides and Other Heavy Atoms

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Sr. Investigator(s):	
Students:	2 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$135,000

PROGRAM SCOPE

This program focuses on the methodological development and computational implementation of quantum chemistry methods for the accurate calculation of electronic structure and properties of molecules, solids, and surfaces, which contain actinides and other heavy atoms.

FY 2012 HIGHLIGHTS

Our support under the HEC program is now in its 11th year. During this time, **39** publications have acknowledged DOE-HEC support under grant No. DE-FG02-04ER15523. During FY 2012, we have continued to focus our attention on methodological developments and their application to actinide systems. We continue to develop and improve computational tools that enable our focused applications on actinide systems. During this grant period, we have investigated a novel approach for using multideterminants in Quantum Monte Carlo. The main thrust of our research effort is more accurate simulations of actinides and derivatives in solid state, interpretation of data, and collaborations with experimentalists.

The Synthesis, Structures, and Chemical Properties of Macrocyclic Ligands Covalently Bonded into Layered Arrays

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Principal Investigator:	Clearfield, Abraham
Sr. Investigator(s):	
Students:	0 Postdoctoral Fellow(s), 2 Graduate(s), 1 Undergraduate(s)
Funding:	$60,000

PROGRAM SCOPE

The United States Department of Energy's Office of Nuclear Energy is developing advanced technologies for treating spent nuclear fuel to recover valuable energy which constitutes 95% of the usable total initial energy. Closing this nuclear fuel cycle poses many challenges, one of which is found in the waste streams that contain trivalent lanthanides and actinides. A key separation is that of americium from curium in order to reduce the long-term radiotoxicity of the waste. We have developed a remarkable ion exchanger that is not selective for univalent, is moderately selective for divalent ions, and highly selective for 3+ and 4+ ions.

The ion exchangers are zirconium or tin complexes of monophenylphosphonate phosphates of general composition $M(IV)(O_3PC_6H_4PO_3)_{1/2}(O_3POH)\cdot nH_2O$. The phosphate proton is the exchange site. Preliminary tests with lanthanides (3+) at pH 3 yields k_d values 10^4-10^6 ml/g. Similar values were obtained for Am^{3+}. A method had been developed to oxidize Am^{3+} to AmO_2^+ and stabilize it for at least 5 days using $Na_2S_2O_8$ in O.1 M $HClO_4$ at 80°C as the oxidizing agent and OCl^- as the stabilizing agent. K_d values for AmO_2^+ with the phosphonate-phosphate exchanger were less than 100 ml/g. Subsequently, we demonstrated a separation factor of 20 for a mixture of AmO_2^+ and Cm^{3+}. We are confident that this value can be greatly improved by optimizing conditions, as this work was all proof-of-concept, first attempt research.

Exchange of Ln^{3+} trended with pH and showed quantitative removal from solution at pH 3 with K_d values of 10^4-10^6 ml/g. Complete recovery of the lanthanides occurs at pH values below 1. Because the early transuranics have several accessible oxidation states, we shall proceed to perform a separation of the early actinides from the lanthanides by a combination of oxidation and pH.

Ion Pair Receptors: Fundamental Studies and Tests Involving Sulfate Anion and Thorium Cation Extraction

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Sr. Investigator(s):	
Students:	1 Postdoctoral Fellow(s), 2 Graduate(s), 1 Undergraduate(s)
Funding:	$165,000

PROGRAM SCOPE

This project is concerned with the synthesis and study of so-called ion pair receptors. Ion pair receptors are systems that bind concurrently both anions and cations within a single molecular framework. Within this broad paradigm, particular emphasis will be placed on neutral systems that (1) bind alkali halide salts (MX) with high specificity, (2) permit the liquid-liquid extraction-based removal of sulfate from nitrate-rich mixtures, and (3) act as indicators and extractants for the thorium(IV) cation. Ultimately, our goal is to be able to recognize, sense, extract, or separate any combination of anion or cation, or mixtures thereof, that are of interest to the DOE mission.

Because it is most fundamental to understanding the difference between an ion pair receptor and a so-called dual host strategy, wherein a mixture of individual cation and anion receptors is employed for recognition and extraction, most of the emphasis to date has been on exploring in detail how changes in structure modulate the recognition of alkali halide salts (Objective 1 above). Here, a particular emphasis is being placed on ion pair receptors that allow for the binding and release of the cesium cation since this is a species of particular current interest in light of the Fukushima disaster.

FY 2012 HIGHLIGHTS

As implied above, the bulk of our activity during FY 2012 has centered around the problem of creating a new class of switchable ion pair receptors that permit the cesium cation to be captured either in bulk media or via extraction and then released easily. The need for release is clear when a problem such as removal of radioactive cesium from water is considered; to be viable, a receptor system not only has to bind the target cation (cesium) and, presumably, the dominant anion (chloride), but also release it after performing the desired function (e.g., separation via liquid-liquid extraction); otherwise the system has little change of being economically viable. We have been collaborating with Dr. Moyer and his group at ORNL to achieve this goal. These efforts recently culminated in the creation of a crown-5 strapped calixarene-calixpyrrole hybrid (*J. Am. Chem. Soc.* 2012, *134*, 1782). The crown-5 calixarene subunit is selective for the potassium cation over the cesium cation. However, the chloride anion salt, Cs^+, is also bound by the receptor (via the calixpyrrole). The resulting ion pair complex can be extracted from aqueous media into an organic solvent. Exposure to the K^+ cation induces ion metathesis and releases the Cs^+ cation. A simple aqueous wash then regenerates the free receptor. The net result is a system whose function, cesium capture and release, can be controlled at will. Current work is focused on extending this principle to other design motifs and to exploring in detail how changes in structure are manifest in function. Achieving alternative ion pair selectivities (beyond CsF and KF) is also a goal.

Controlling Actinide Hydration in Mixed Solvent Systems: Towards Tunable Solvent Systems to Close the Nuclear Fuel Cycle

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Sr. Investigator(s):	
Students:	1 Postdoctoral Fellow(s), 2 Graduate(s), 1 Undergraduate(s)
Funding:	$150,000

PROGRAM SCOPE

The overall goal of this project is to integrate experimental methods to directly probe the hydration and covalency of the f-element cations in aqueous and mixed solvent electrolyte systems. We are accomplishing this goal using traditional thermodynamic methods and advanced spectroscopic tools to explore the effect of solvent properties, cationic radius, and covalency for the f-element cations on solubility, hydration, and coordination chemistry for solution species. To date, we have focused primarily on complexation of the lanthanide cations by the hydroxycarboxylate ligands α-hydroxyisobutyric acid (HIBA) and 2-hydroxy-2-methylbutanoic acid (HMBA) in solutions of water + methanol. We are measuring stability constants, enthalpies, and entropies of complexation using potentiometry, NMR, UV-VIS spectroscopy, and calorimetry. In addition, we are collaborating with computational chemists on the role of methanol in the hydration of the lanthanide cations. In addition, we are relating the effects of methanol:water on the chromatographic separations of the trivalent lanthnides, actinides, and the Group II cations.

FY 2012 HIGHLIGHTS

We have completed thermodynamic and spectroscopic studies on the complexation of the lanthanides, uranyl, and thorium with HIBA and HMBA while varying the mole fraction of methanol:water for the solvent. In addition, we have investigated the impact of methanol on the separation of the trivalent actinides and on the hydrolysis products of the divalent beryllium cation.

Origin of Actinide Ion Partitioning in Biphasic Systems

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Sr. Investigator(s):	Corrales, L. Rene, Arizona, University of
Students:	0 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding:	$200,000

PROGRAM SCOPE

The goal of this program was to use multiscale theoretical methods to characterize the molecular structure and dynamics of solvated actinide (An) metal cations and their ligated complexes, as well as the organic:water interfacial structure as these solutes migrate across the phase boundary. All calculations were performed in the infinite dilution limit. Significant progress was made in the objectives of the proposal. Not only have we derived new insight into the thermodynamic favorability of various extraction mechanisms and the role of solvent organization upon ion reactivity, but we have also developed new theoretical models and analyses that have a broad impact upon the simulations community.

Specific deliverables include (1) pinning down the structural and thermodynamic properties of U, Np, Pu in (III-VII) oxidation states via calculated thermodynamic data and simulated XANES spectra; (2) determining the thermodynamic end-products of acetylacetone complexation of Np(III-VI), and the thermodynamics of extraction into alkanes and alcohols as a function of oxidation state and dielectric constant; (3) determining thermodynamic favorability of ion-pair and solvent-separated ion pair formation as a function of dielectric constant for lanthanide(III) chloride solutions, which mimic An(III) chloride solutions; (4) benchmarking DFT methods for calculating thermodynamics of solutes in aqueous and organic phases (we determined that no currently available density functionals can reproduce liquid phase organic solvents using cluster models); (5) determining the role of solvent packing ability upon the physical properties of aqueous:organic interfaces; and (6) developing new methodology for characterizing role of solvent upon ion (both cation and anion) reactivity in single and dual-phase systems.

Since a major aspect of the proposed work has been focused upon MD simulation, a need arose to be able to rapidly analyze the solvent structure about an ion and to be able to perform the necessary statistical analyses to investigate whether solvent organization is related to the reactivity of the ion in solution. Toward this end, the *moleculRnetworks* series of processing scripts has been developed (written in the statistical computing language R).

An Integrated Basic Research Program for Advanced Nuclear Energy Separations Systems Based on Ionic Liquids

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Students:	0 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$200,000

PROGRAM SCOPE

Advanced nuclear energy systems and fuel cycles are being proposed to address the world's increasing energy needs while avoiding major environmental impacts and proliferation of nuclear materials. Ionic liquids (ILs) are proposed as tunable solvents for processing and recycling of radionuclides and are meeting these challenges, as these new solvents offer non-volatility, non-flammability, high conductivity, wide electrochemical windows, superior extraction performance, radioprotection of extracting agents, and the suppression of the third phase formation. This application involves exposure of the solvent to radiation generated by decaying radionuclides. Our goal is to establish the fundamental radiation chemistry of IL-based solvents in order to guide rational design of extraction systems that minimize material degradation and loss of separations efficacy with cumulative radiation dose. Spectroscopy, product analyses, measurements of partitioning coefficients, and other methods are used to this end. Mechanistic insights reached in our studies guide the development of separations chemistry by our SISGR members at other institutions.

FY 2012 HIGHLIGHTS

We have designed radiation-resistant ILs and tested their performance. Our studies indicate that the main cause for rapid radiolytic degradation of ILs was oxidative fragmentation of their constituent anions. We discovered two classes of exceptionally resilient anions—conjugate bases of superacids—that were also sufficiently hydrophobic, which made them suitable as diluents for nuclear separations that can be used across a wide range of extraction conditions. These classes are aromatic imide anions, such as saccharinate, and certain polycyanide anions, such as 1,1,2,3,3-pentacyanopropenide. These resilient anions do not fragment in their reduced, oxidized, and electronically excited states. Another important milestone is our discovery of general methods for stabilization of organic cations. The key to this stabilization was using modifying arms that yield stable carbocations upon carbon-heteroatom bond scission of the electronically excited cation; such carbocations can react back with the released base regenerating the parent cation in geminate pairs. While this modification was expected to decrease the stability of the redox states of these cations, we have demonstrated that for certain cations this anticipated decrease does not occur due to electron and hole (electron deficiency) delocalization through the formation of pi-electron sandwich dimer radical ions. For cations that do not exhibit such delocalization/stabilization, we have found ways to divert the redox reactions towards the resilient anionic constituents thereby avoiding cation fragmentation. Our product analyses fully corroborate these mechanistic insights reached by spectroscopic means. Our studies provide the sufficient background required to reach our grand goal of designing IL systems that exhibit no significant deterioration of their chemical and physical properties over the expected life cycle of the extraction solvent.

Heavy Element Chemistry

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	Skanthakumar, S., Argonne National Laboratory
	Wilson, Richard, Argonne National Laboratory
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	Jin, GengBang, Argonne National Laboratory
Students:	3 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$3,035,000

PROGRAM SCOPE

This program seeks to provide the fundamental knowledge of heavy-element chemistry necessary to form the basis for a predictive understanding of their environmental fate, and their role in advanced nuclear energy technologies. Our efforts are expressed in four integrated subtasks: electronic properties, actinide ligand interactions, structured phases and interfaces in separations science, and the synchrotron program (actinide facility) supporting all the programmatic research.

Our interests focus on interactions that range from the atomic to the collective scales. At the atomic level, our studies explore electronic properties with physical influences on bonding behaviors, energy changes, and energy partitioning that includes phonon and confined-space effects. Single-ion properties such as crystal-field splittings, formal potentials, optical behavior, and magnetic response are quantified in detail. Complementing these atomic-scale studies are our efforts to understand molecular-level organization of f-ion solutes and the structures of solid phases that form from their solutions. These structural studies are informing efforts to map large thermodynamic databases onto the molecular scale. On intermediate-length scales, we are characterizing solute and solvent organizations of supramolecular or nanoscale aggregates that can have a marked impact on physical properties exhibited by 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. Studies of solvent organization, which can include the formation of ion pairs, reverse micelles, and third-phases, are providing insight into how to model and use this organization to optimize separations in complex systems. These studies are enhanced by our Advanced Photon Source efforts, which center on the development of synchrotron-based experiments and their application to problems of interest and importance to the broader actinide community.

FY 2012 HIGHLIGHTS

Significant effort this year has focused on developing a metrical description of metal speciation relevant to liquid-liquid extraction processes. Experiments have been undertaken to probe f-ion coordination environments in both aqueous and organic solutions over length scales that range from the atomic to the mesoscopic. Critical to these efforts have been synchrotron-based scattering and spectroscopy experiments providing unprecedented structural details. Linking inner- and outer-sphere coordination complexes in aqueous solutions with published thermodynamic data is providing theorists with detailed structure-energetics relationships unavailable before these studies. Observing the formation and structures of complex nano- and mesoscale aggregates and their correlation with extraction efficacy is providing new insights into the complex impact of longer-range molecular correlations on chemical separations. Complementing these efforts is a new program probing molecular-level correlations at water/vapor interface.

Understanding Actinide Aggregation

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Students:	1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$744,000

PROGRAM SCOPE

The ultimate goal of the proposed work is the development of a predictive understanding for the formation, structures, stabilities, and reactivities of complexed actinide aggregates that form under conditions relevant to the reprocessing of spent nuclear fuel. Insight is sought to inform the design of separations processes specifically targeting such species. To accomplish this goal, a multifaceted approach combines new advances in the experimental determination of metal-ion speciation, coordination, and stability in solution with recent developments in computational chemistry including electronic structure theory. This powerful combination of technical capabilities will permit the acquisition of new metrical information relevant to the solution chemistry underlying actinide aggregation. The results will provide a framework upon which to build a predictive understanding of the chemical energetics driving actinide cluster formation. Ultimately this approach will afford new insights and theories of actinide nanophase formation that will form the basis upon which to design new approaches to separating aggregated metal-ion species within the context of advanced nuclear energy systems. Within a broader context, the development of a fundamental understanding of the chemistry underlying nanophase formation, structure, stability, and reactivity will have an impact on technological advances across broad areas of current interest including catalysis, photonics, targeted materials synthesis, and the modeling of environmental contaminant transport.

FY 2012 HIGHLIGHTS

Three structures composed of the same octahedral aggregates $[Th_6(OH)_4O_4]^{12+}$ have been isolated. The fundamental cationic, hexameric unit was crystallized with a series of three carboxylate functionalized ligands decorating the surface and serving as charge-balance anions. Their presence in solution is confirmed by high-energy x-ray scattering data. Although the proton positions were not directly determined in the crystal-structure refinement, charge balance dictates the stoichiometery of four μ_3-hydroxo and four μ_3-oxo bridges. Supported by accompanying electronic calculations, done at the DFT level, the structural and spectroscopic studies place the oxo-bridged ligands in a tetrahedral arrangement on the faces of the cluster core, which maximizes their distances as well as the symmetry of the cluster. The DFT calculations agree with the assignment of the proton positions found from the chloroacetate crystal structure. Raman and proton NMR spectra were extracted from the calculations and used to guide experimental peak assignments. The average water complexation energies, the gas phase, and the aqueous and DMSO acidities were predicted; and the Th clusters are found to be mild to strong acids in gas phase with some acidities in the range of 250 to 270 kcal/mol; yet they behave as weak acids in solution. The acidities of the model $Th_6(OH)_4O_4O_6$ complex have been calculated, and these complexes are predicted to be very strong gas phase acids.

An Integrated Basic Research Program for Advanced Nuclear Energy Separations Systems based on Ionic Liquids

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Sr. Investigator(s):	
Students:	2 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding:	$551,000

PROGRAM SCOPE

Future advanced nuclear energy systems will require significant changes in the way nuclear fuel is processed to achieve the increases in efficiency and reductions in waste sent to repositories that are necessary if nuclear power is to play a major role in serving the world's growing energy needs. We expect that ionic liquids (ILs, salts that melt at low temperatures) 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 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, 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 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 have smaller environmental impacts, bringing us closer to a sustainable energy future.

FY 2012 HIGHLIGHTS

We demonstrated promising approaches to radiation resistant ionic liquids. Selected dialkylimidazolium bistriflylimide salts were exposed to Co-60 gamma radiation doses up to 2 MGy, and the radiolysis products were identified using liquid chromatography and mass spectrometry. Specific damage locations were located and quantified using site-specific deuteration. Several previously unknown and potentially metal-coordinating products were found. The presence of oxygen reduced the yield of these products, while increasing water content favored their formation. Ionic liquids with substitutions that block the reactive C-2 carbon site prevented formation of these products and demonstrated enhanced radiation stability. In other preliminary work, the addition of aryl moieties, such as the benzyl group, to various cation motifs was shown to reduce radiation damage. More detailed studies are underway.

Renewal of Support for the ACS Summer Schools in Nuclear and Radiochemistry

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Sr. Investigator(s):	
Students:	0 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$163,000

PROGRAM SCOPE

The Summer School in Nuclear and Radiochemistry (NCSS) had been funded by the U.S. Department of Energy and the American Chemical Society (ACS). In the past year, however the ACS has reduced its active financial support. NCSS is a highly competitive program drawn from an elite group of STEM (science, technology, engineering, and mathematics) undergraduates. Each summer, 24 students are selected to participate in the NCSS program; half are placed at Brookhaven National Laboratory (BNL) and the other half at San Jose State University (SJSU). Typically, the applicant pool annually ranges around 120 prospective junior and senior undergraduates drawn from physics, chemistry, and associated majors. Students are awarded a stipend, full travel and housing expenses, as well as a tuition waiver for their participation. They receive course credit—3 credits for lecture (CHE-361) and 3 for laboratory (CHE-362) course components. Students reside at SJSU or BNL and attend 3 hours of lecture per day, 5 days per week; complete 10 laboratory modules involving nuclear instrumentation and various radiochemical techniques; participate in field trips to regional scientific, medical, and nuclear facilities (e.g., Sloan Kettering Cancer Center, Entergy Indian Point Nuclear Power Plant, etc.); and participate in special topic seminars and symposia related to nuclear science topics (e.g., nuclear forensics, nuclear medicine, nuclear proliferation policy, etc.). Grades are based on four major exams, lab reports, class participation, a term paper on a topic of the student's choosing, and an oral presentation on that topic.

FY 2012 HIGHLIGHTS

The Department of Energy's Office of Basic Energy Sciences renewed the proposal for FY 2012, with contributions from Nuclear Physics. The programs held during the summer of 2012 were the first of the five years committed under the renewed grant. They ran smoothly and successfully.

Actinide Chemistry

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Sr. Investigator(s):	Andersen, Richard A., Lawrence Berkeley National Laboratory Booth, Corwin H., Lawrence Berkeley National Laboratory Rao, Linfeng, Lawrence Berkeley National Laboratory Raymond, Kenneth N., Lawrence Berkeley National Laboratory Gibson, John, Lawrence Berkeley National Laboratory Nitsche, Heino, Lawrence Berkeley National Laboratory Gregorich, Kenneth, Lawrence Berkeley National Laboratory
Students:	6 Postdoctoral Fellow(s), 3 Graduate(s), 0 Undergraduate(s)
Funding:	$3,000,000

PROGRAM SCOPE

Berkeley Lab actinide research supports the role of the U.S. Department of Energy (DOE) as the 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 fundamental heavy element chemistry and physics at the atomic and molecular levels, and using this knowledge to address issues in actinide science. A central theme is f-orbital bonding and its impact on actinide chemistry and physics. Collaborative research ranges from exploring gas-phase actinide chemistry, to investigating f-element bonding in actinide materials, to elucidating electronic and magnetic characteristics of actinide molecules. Specific topics, including actinide complexation and 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 and calorimetry, and make intensive use of 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 DOE in actinide science.

FY 2012 HIGHLIGHTS

- Transuranic Coordination Chemistry
- Organometallic Chemistry
- Strongly Correlated f-Electron Molecular Systems
- Electronic Structure and Surface Chemistry of Actinides Using Soft X-Ray Synchrotron Radiation
- Actinide Solution Chemistry: Chemical Thermodynamics and Structure of Actinide Complexes
- Heavy Element/Nuclear Radiochemistry Program

Meeting the Challenges Posed by Advanced Nuclear Energy Systems: Understanding and Controlling Actinide and Fission Product Chemistry and Radiation Effects in Actinide Materials

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Sr. Investigator(s):	Andersen, Richard A., Lawrence Berkeley National Laboratory Booth, Corwin H., Lawrence Berkeley National Laboratory Gibson, John K., Lawrence Berkeley National Laboratory Lukens, Wayne W., Lawrence Berkeley National Laboratory Rao, Linfeng, Lawrence Berkeley National Laboratory Raymond, Kenneth N., Lawrence Berkeley National Laboratory
Students:	4 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$814,000

PROGRAM SCOPE

This research encompasses a range of research needs necessary to create advanced energy technologies. In particular, it addresses those needs described in the BES report "Basic Research Needs for Advanced Nuclear Energy Systems," which presented the following Scientific Grand Challenges: (1) resolving the f-electron challenge to master the chemistry and physics of actinides and actinide-bearing materials, (2) understanding and designing new molecular systems to gain unprecedented control of chemical selectivity during processing, and (3) developing a first-principles description of mechanical properties of multi-component, multiphase systems under extreme conditions. Meeting these challenges will require fundamental advances in understanding the bonding of actinide compounds and in understanding and controlling the problematic behavior of actinides and fission products under a wide range of conditions. The proposed research program provides these advances through a series of interrelated research thrusts: better understanding of f-orbital bonding, exploiting f-orbital bonding for improved separations, controlling the chemistry of the problematic radionuclides ^{237}Np and ^{99}Tc, and experimentally quantifying radiation damage in actinide materials to compare these quantities to theory.

FY 2012 HIGHLIGHTS

- Understanding f-Orbital Bonding
- Exploiting f-Orbital Bonding in Separations Biomolecule Energetics
- Understanding and Controlling the Redox Chemistry of Tc
- Quantifying Radiation Damage

Early Career - Molecular Transuranic Discovery Science: Underpinning National Energy Security and Waste Remediation Needs

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Sr. Investigator(s):	
Students:	0 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$500,000

PROGRAM SCOPE

The aims of this research are to advance knowledge and understanding of transuranic (primary focus is upon plutonium) coordination chemistry, electronic structure, and bonding. 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. Certain soft donor ligands have shown exceptional selectivity for trivalent actinide ions over trivalent lanthanide ions, but the reason for this selectively is not known. A central goal is to decipher the extent to which covalent bonding interactions are important in soft donor ligand complexes, the nature of valance f and d orbital participation, the differences between actinide and lanthanide bonding, and the trends across the actinide series. The chemistry of hard oxygen donor ligands, and how they bind to actinide ions, is also vital to a number of proposed actinide separation schemes. Acquiring such detailed bonding understanding will ultimately facilitate rational molecular design processes for novel chemical solutions to nuclear fuel cycle challenges.

FY 2012 HIGHLIGHTS

A suite of actinide and lanthanide complexes with selenium soft donor models of sulfur donor minor actinide extractants have been synthesized, isolated, characterized, and structurally determined. The results shed new understanding on the fundamental chemical bonding origin of actinide selectivity of soft donors and support the hypothesis of increased covalency in the 5f versus 4f bonding. The chemistry of hard oxygen donor diglycolamides was advanced, leading to the first structurally determined complex of plutonium with this class of separation agent and helping to unravel the complicated behavior observed in actinide solvent extraction tests. New starting materials for advancing nonaqueous plutonium chemistry have also been developed. The research in FY2012 has resulted in several high-quality international peer-reviewed chemistry journals including *Chemical Communications* and *Inorganic Chemistry*. An invited review article was also accepted to the highest impact factor journal in chemistry, *Chemical Reviews*, for a special 2013 nuclear chemistry topical issue.

Heavy Element Chemistry

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	Conradson, Steve, Los Alamos National Laboratory
	Martin, Rich, Los Alamos National Laboratory
	Batista, Enrique, Los Alamos National Laboratory
	Kozimor, Stosh, Los Alamos National Laboratory
	Boncella, James, Los Alamos National Laboratory
Students:	2 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$1,325,000

PROGRAM SCOPE

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, chemical reactivity, and thermodynamic properties. Studies are directed at understanding covalent mixing in metal-ligand bonding in light actinide complexes through a combination of synthesis, spectroscopy, 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. These studies employ a range of spectroscopic, electrochemical, and structural methods including x-ray and neutron diffraction, x-ray absorption, nuclear magnetic resonance, electronic absorption and emission, infrared and Raman, magnetic susceptibility, etc. These experiments rely on both existing Los Alamos National Laboratory facilities and other DOE user facilities (e.g., SSRL, ALS, APS, LANSCE). The synthesis and characterization studies are closely coupled to the use of hybrid density functional theory (DFT) for examination of the electronic structure in both molecular and solid state systems.

FY 2012 HIGHLIGHTS

Recent synthetic highlights include direct synthetic routes to mono and bis imido [$U^{IV}(NR)^{2+}$ and $U^{V}(NR)_2{}^{+}$] functionalities; development of new starting materials for Th, U, Np, and Pu chemistry; and synthesis of functionalized dithiophosphonate anions and metal complexes to understand the effects of covalent mixing in actinide/lanthanide separations. Recent spectroscopic highlights include the direct observation of the ^{239}Pu nuclear magnetic resonance (NMR) transition; O, Cl, and S K-edge x-ray absorption spectroscopy (XAS) to determine the extent of orbital mixing in actinide metal-ligand bonds; and luminescence in $NpO_2{}^{2+}$ and $PuO_2{}^{2+}$ complexes to understand trends in electronic structure and bonding within the linear trans dioxo ions (U, Np, Pu). Theoretical studies have calculated orbital mixing in metal-ligands bonds for comparison with XAS, and employed time-dependent density functional theory (TD-DFT) to aid in assignment of electronic transitions and to simulate spectra both valence (optical) and core (ligand K-edge) electron transitions. Screened hybrid density functional theory has been used to study the effects of spin-orbit coupling on the light actinide dioxides (Th, Pa, U, Np, Pu, and Am).

An Integrated Basic Research Program for Advanced Nuclear Energy Separations

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Funding:	$207,000

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 James Wishart at BNL that lies in the development of ionic-liquid systems for separation of fission products.

FY 2012 HIGHLIGHTS

We herein report the achievement of enhanced extractabilities and selectivities for separation of rare earth element (REEs) using di(2-ethylhexyl) phosphate (DEHP)-based ionic extractants in 1-hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide [C6mim][NTf_2]. This work highlights the potential of developing a comprehensive ionic liquid-based extraction strategy for REEs using ionic liquids as both extractant and diluent.

Influence of Solution Phase and Interfacial Structure on the Stability of Actinide Oxidation States: A Computational Chemistry Approach

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Funding: $295,000

PROGRAM SCOPE

Subsurface migration of radioactive waste resulting from nuclear energy and weapons production is a critical issue to the U.S. Department of Energy (DOE), and the safe and cost-effective disposal of this waste could be a limiting factor in deploying new energy technologies for the nation. Molecular-level processes, such as aqueous complexation, adsorption, and the reduction/oxidation chemistry of actinide species at mineral interfaces, often control the complex transport and reactive behavior of these species in chemically and physically heterogeneous subsurface environments. 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.

The ultimate goal of our program is to develop a fundamental understanding of actinide redox chemistry under experimentally relevant conditions using a combination of statistical and quantum mechanical methods. Our models aim to understand the role of the 5*f*-electrons and the local molecular environment on the oxidation state of actinides; the speciation, hydrolysis, and bonding of actinides in complex solution environments; and the adsorption, incorporation, and reduction of actinides on mineral surfaces with surface defects, charge states, and coordination environments.

FY 2012 HIGHLIGHTS

We were able to predict the thermodynamics of hydrolysis for uranium by calculating the first acidity constant (pKa) for uranium in various oxidation states, and predict the unknown pKa for UO_2^+. Good agreement was found between the experimental and our calculated acidity constants (pKa) of U_4^+ and UO_2^{2+}, which gives us confidence in the accuracy of our prediction. We also obtained accurate activation energies and determined the mechanisms of water exchange between the first and second hydration shells of UO_2^{2+}. On the basis of the free energy differences and activation barriers, we predict the dominant exchange mechanism between $[UO_2(OH_2)_5]^{2+}$(aq) and bulk water is dissociative.

We developed models describing the interaction and potential reduction of UO_2^{2+} on mineral surfaces and compared them to available experimental observations. On alumina, we found that direct absorption of the actinide to the surface will be more favorable in acidic environments (low pH) and that this is strengthened on deprotonated surfaces. On a reducing Mackinawite, we found that uranium is reduced from a U(VI) to U(V) but not U(IV), while it does not directly bind with the surface.

Photosynthetic Systems

Institutions Receiving Grants

Chlorophyll Synthesis and Stability in Cyanobacteria

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Funding:	$170,000

PROGRAM SCOPE

The theme of the project is to start understanding the process of thylakoid biogenesis and particularly the proteins involved in this process. This is critical because photosystems, a key part of the photosynthetic apparatus, are located in thylakoid membranes; but very little is known about how these membranes originate and what determines the degree of thylakoid biosynthesis. If we were to be able to modify thylakoid amounts in cells, we could change the light absorption cross section per cell and the amount of energy and reducing power that is available to the cells. We study this process in the cyanobacterium *Synechocystis* sp. PCC 6803 because this organism readily can be modified genetically, and cyanobacteria are the evolutionary precursors to chloroplasts. A number of proteins had been identified in the project proposal to be studied in this project. In some cases, the corresponding genes are being deleted. However, if there is reason to believe that deletion of a gene would be lethal to the cells and therefore no full segregants can be obtained, then we focus on overexpression of this gene. Based on the results thus far, we have not yet identified a single gene that is a key modulator or regulator of thylakoid membrane biogenesis; but other interesting phenotypes have resulted that are now being studied.

FY 2012 HIGHLIGHTS

This year we have overexpressed four proteins in *Synechocystis* and deleted one. The amount of chlorophyll per cell, the ultrastructure of the cell (determined by electron microscopy), and the viability of the mutants were normal, suggesting that thylakoid membrane biogenesis was not greatly affected by these proteins. However, overexpression of some of these proteins modulated survival of *Synechocystis* cells at increased temperature or after heat shock. Whether this is due to a general chaperone nature of some of these proteins or to interaction of these proteins with thylakoid membrane processes remains to be established. However, it is clear that the physiology of the cyanobacterium can be modulated significantly by our approach. We also have generated some of these mutations in a background strain that can synthesize chlorophyll only in the light. Interestingly, in at least one of the cases, the amount of chlorophyll per cell was reduced significantly relative to the background strain; and thylakoid membrane amounts were reduced as well. The molecular mechanism for these phenomena is now being investigated.

Structure and Assembly of Rubisco Activase

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Funding:	$195,000

PROGRAM SCOPE

In higher plants, the P-loop ATPase Rubisco activase (Rca) helps coordinate the light and dark reactions of photosynthesis by catalyzing the release of inhibitors from Rubisco. When ATP levels drop or the temperature rises, Rca activity falls off, Rubisco becomes inactivated, and atmospheric carbon fixation ceases. The first goal of this project is to understand the structural basis of energy conversion mediated by ATP hydrolysis. The second goal of this project is to characterize the physical interaction of Rca with its partner protein Rubisco.

FY 2012 HIGHLIGHTS

We have used x-ray crystallography to show that the Rubisco recognition site on Rca involves an insertion into the canonical AAAplus domain that places the specificity-determining residues around the periphery of ring-like assemblies. We have utilized thermostability assays to demonstrate that ADP stabilizes Rca more significantly than ATP, that magnesium ions have a destabilizing effect on ADP-bound Rca, and that phosphate ions provide weak stabilization of the ADP-bound form of Rca. Using fluorescence correlation spectroscopy, we have determined that ADP-bound Rca self-associates in a step-wise fashion to form oligomeric and higher-order forms from dimeric building blocks.

Protein Targeting to the Chloroplast Thylakoid Membrane: Structure and Function of a Targeting Complex

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Funding:	$165,000

PROGRAM SCOPE

Chloroplast thylakoid membranes are the site of photosynthetic electron transport and therefore represent the primary energy-generating membranes in plants and algae. Biogenesis of light capturing membrane protein complexes that power electron transport relies on evolutionarily conserved protein routing/insertion machinery to target both nuclear and chloroplast encoded proteins to the thylakoid membrane. For example, two evolutionarily conserved GTPases, **S**ignal **R**ecognition **P**article (SRP) and its receptor, target light-harvesting chlorophyll a/b-binding proteins (the LHCs) to the thylakoid membrane where they are inserted by Albino3 (Alb3). The importance of this targeting/insertion mechanism is underscored by the fact that LHCs bind 30-50% of the chlorophyll responsible for photosynthetic light capture in mature chloroplasts and are the most abundant membrane proteins in the world. The overall goal of our studies is to understand the mechanism by which LHCs are targeted to the thylakoid membrane by SRP and its receptor. Results of our work may also aid in better understanding a homologous protein targeting/insertion pathway in bacteria that is being developed for production of biofuels.

Our studies are focused on the role of cpSRP43, which lacks GTPase activity but appears to coordinate the order and timing of targeting events in solution and at the membrane through its interactions with LHC targeting substrates, the GTPase components, and the Alb3 insertase. We hypothesize that binding of cpSRP43 to the C-terminus of Alb3 is the primary interaction responsible for directing a cpSRP/LHC/cpFtsY membrane-associated targeting complex to Alb3. We also hypothesize that cpSRP-Alb3 binding serves to trigger LHC release from cpSRP and initiate disassembly of the targeting complex for cpSRP/cpFtsY recycling. Biochemical and biophysical studies published during this grant cycle demonstrated that cpSRP-Alb3 interaction triggers LHC release from cpSRP and initiates GTP hydrolysis by SRP and its receptor, indicative of targeting complex disassembly for recycling of targeting components.

FY 2012 HIGHLIGHTS

Structural studies are being used to elucidate the cpSRP43-Alb3 interface in order to understand structural changes that occur in cpSRP43 to facilitate LHC release from cpSRP. Complimentary biochemical studies are examining whether LHC release from cpSRP requires GTP hydrolysis or whether LHC release from cpSRP is an event needed to trigger GTP hydrolysis and subsequent recycling of the targeting components. Completion of the proposed studies will provide structural and functional details that are missing in our understanding of membrane events required for LHC insertion.

Chloroplast Antisense RNAs and Post-Transcriptional Gene Regulation

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Funding:	$159,174

PROGRAM SCOPE

This project is focused on a previously unrecognized mode of gene regulation in chloroplasts—antisense RNAs that are encoded by the chloroplast genome. The chloroplast is the site of photosynthesis and expression of its genes is essential. In other organisms, antisense RNAs can either promote or interfere with gene expression, so we hypothesize that such a regulatory system also exists in chloroplasts. The project uses two parallel approaches to address this hypothesis. The first is a high-throughput sequencing approach, to discover and characterize these antisense RNAs. The second is a functional approach, to identify specific regulatory targets.

FY 2012 HIGHLIGHTS

In our first approach, we collaborated with another BES project to identify over 100 new antisense RNAs in the chloroplast. These varied greatly in size and abundance, and based on their sequences, potential targets included RNA maturation, protein synthesis, and RNA stability. They were derived from all parts of the chloroplast genome, and some are conserved between species. In our second approach, we discovered that many more than 100 antisense RNAs are synthesized but most are rapidly removed by a chloroplast enzyme called Ribonuclease J. When we depleted chloroplasts for RNase J, there was a massive accumulation of antisense RNAs, which essentially shut down gene expression by forming duplexes with RNAs that should be translated into protein. Given that embryo development requires chloroplast gene expression, our results explain why RNase J is an essential enzyme for plants.

Regulation of Plant Cells, Cell Walls, and Development by Mechanical Signals

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Funding:	$230,000

PROGRAM SCOPE

Recent evidence demonstrates that cells in the plant *Arabidopsis thaliana* respond in several critical ways to mechanical stress. One is that the cytoskeletal microtubules of the cells align parallel to the principal direction of anisotropic stress, and another is that the efflux carrier for the plant hormone auxin distributes within the plasma membrane proportionally to the mechanical stress applied by each neighboring cell. Together these properties promise to explain a number of phenomena that are not yet understood and have a central role in the developmental behavior of plant cells and in the deposition of their cell walls. This includes the determination of the plane of the next cell division (as the microtubule array specifies this) and the determination of the direction in which cellulose fibrils are deposited in forming cell walls (as the cellulose synthase complexes are directed by microtubules). Cellulose fibril deposition is expected then to reinforce the cell wall and thereby change the pattern of cellular expansion. As expansion creates the mechanical stress on neighboring cells, the direction of cellulose deposition will affect the planes of cell division in the next cellular generation as well as the direction of subsequent cellulose biosynthesis and auxin flow. The interaction of chemical (auxin) and mechanical signals is therefore expected to determine plant cell and tissue behavior, including cell wall biosynthesis.

We are now testing these hypotheses. Experiments are designed to establish the relation and dynamics of the interaction between mechanical stress in its control of microtubule arrays, the relation of stress and microtubules to cellulose synthesis, and the effects of changes in cell wall mechanics on cell division and auxin flow.

FY 2012 HIGHLIGHTS

We have developed a new cell type to use in our studies, the pavement cell, which has optical properties that facilitate live imaging of microtubules and cellulose synthase complexes. With it we have shown that the microtubules, like those of the shoot apical meristem used in the earlier studies, respond to changes in physical stress, whether due to cell ablation, compression in a newly designed microvise, or suppression of cellulose synthesis. We have also measured microtubule severing before and during mechanical stress, and the responses of cells with severing mutants, which shows severing to be important for stress-based reorganization. We have made plants whose cell wall properties are altered by mutants in cellulose synthase genes and in cellulose synthase-like genes thought responsible for production of other cell wall components, and have locally altered the mechanics of cell walls with expansins, cellulase, and various types of pressure probes. We have followed microtubule organization and auxin efflux carrier localization before, during, and after these treatments.

Early Career: Engineering Self-Assembled Bioreactors from Protein Microcompartments

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Funding:	$159,224

PROGRAM SCOPE

The goal of our work is to engineer robust protein organelles capable of catalyzing novel chemical reactions.

FY 2012 HIGHLIGHTS

The goal of our work is to understand the assembly, function, and engineering potential of the carboxysome bacterial microcompartment by: (1) using a genetic and cell biological approach to explore the functional role of each component microcompartment protein in the native host *Synechococcus elongatus* and (2) reconstitution of carboxysome formation in a heterologous host as a means of defining the essential molecular features relevant to carboxysome size, shape, and assembly. Together, these approaches aim to define the fundamental principles of carboxysome structure and enable the future engineering of microcompartments with novel function, such as synthetic organelles with enhanced metabolic function.

Initial investigation revealed that a portion of the carboxysome operon from Halothiobacillus neapolitanus was sufficient to yield expression of functional carboxysomes in E. coli. By optimizing operon construct and biochemical protocols, we have demonstrated that E. coli is capable of synthesizing carboxysomes highly similar to the native host. We have also demonstrated that these microcompartments are functional both *in vivo* and *in vitro*.

Dissecting the Function of Immunophilins in the Assembly of Photosynthetic Complexes

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Funding:	$170,000

PROGRAM SCOPE

Originally defined as cellular receptors for immunosuppressants, immunophilins have been identified in a wide range of organisms from bacteria to fungi, plants, and animals. Almost all immunophilins function in protein folding processes as molecular chaperones and foldases. Arabidopsis, a flowering plant with the smallest genome, contains more than 50 genes encoding immunophilins. In particular, 16 immunophilin members are predicted to target chloroplast thylakoid lumen, implicating these proteins in the regulation of photosynthesis. Indeed, genetic and biochemical analyses have demonstrated critical functions for several immunophilins in the biogenesis and maintenance of photosynthetic complexes such as PSII. Studying immunophilins thus provides a unique opportunity to understand the molecular mechanism underlying assembly and maintenance of protein machines involved in photosynthetic light reactions. The long term goal of this project is to understand the regulation of photosynthesis by chloroplast immunophilins. The specific objectives for this funding period will be to dissect the mechanism of action of two thylakoid lumen immunophilins, FKBP20-2 and CYP38, that are involved in the assembly and maintenance of PSII. At the same time, we will expand our effort into the functional analysis of at least one other immunophilin that is required for the accumulation of Cyt b6f complex.

FY 2012 HIGHLIGHTS

(1) Identification of the partner proteins for FKBP20-2 using yeast two hybrid and transgenic lines expressing HA-FKBP20-2.

(2) Structural analysis of CYP38. Cyclophilin 38 (CYP38) is one of the highly divergent cyclophilins from *Arabidopsis thaliana*. Here we report the crystal structure of the AtCYP38 protein (residues 83-437), at 2.39 Å resolution. The structure reveals two distinct domains: an N-terminal helical bundle and a C-terminal cyclophilin β-barrel, connected by an acidic loop. In this structure, N-terminal residues become part of the C-terminal β-barrel, thereby making it an inactive PPIase. Furthermore, the helical domain, although predicted to be similar to leucine zipper, contains several new elements for protein-protein interaction.

(3) Functional analysis of other thylakoid lumen immunophilins. Although we will focus our effort on those members involved in assembly of PSII and Cyt b6f complexes, we will continue the functional analysis of other lumenal immunophilins using genetic and biochemical analysis, as an ongoing effort towards the long-term goal of connecting each thylakoid immunophilin to a specific process in photosynthesis.

Phytochrome from Green Plants: Properties and Biological Function

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Funding:	$160,000

PROGRAM SCOPE

The long-term goal of this program is to define the molecular mechanisms by which the phytochrome (phy) family of sensory photoreceptors perceive and transduce informational light signals to photoresponsive genes in regulating plant growth and development. The central focus of this project is to define the mechanisms by which the phys induce and modulate the shade-avoidance response (SAR) in green plants. Toward this objective, the specific aims for the current funding period are to (1) delineate the biological functions of multiple, previously-identified phy-Interacting bHLH transcription-Factor (PIF)-family members in controlling the SAR, including definition of the scope of functional overlap or redundancy between family members in this process; and (2) identify potential target genes of the PIF transcription factors under shade-avoidance conditions, using genome-wide expression profiling to identify PIF-regulated early-response genes, and (given sufficient time and remaining resources) chromatin immunoprecipitation (ChIP) procedures to identify promoters that are potential direct targets of these phy signaling partners.

FY 2012 HIGHLIGHTS

We have focused on four facets of the program: (1) completion of our investigations of the shade-elicited, genome-wide transcriptional changes induced by the phy system via the PIF1, PIF3, PIF4, and PIF5 transcription factors; (2) assessment of the impact of the negative feedback loop that exists between the PIFs and phyB on the phenotypic responses of seedlings to light and shade; (3) investigation of the role of PIF3 in controlling the oscillations in growth rate that are observed in green seedlings grown under diurnal light-dark conditions; and (4) molecular characterization of a mutant isolated in a novel genetic screen for mutants defective in the shade-avoidance response. All four facets of the project have now resulted in publications.

Energetics and Mechanisms of Protein Transport and Energy Transduction in Chloroplasts

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Funding:	$190,000

PROGRAM SCOPE

Although chloroplasts have been studied extensively for over 70 years, fundamental questions concerning their biogenesis and the reactions of photosynthetic energy transduction remain unanswered. Plastids are capable of synthesizing approximately 100 proteins from DNA in the chloroplast genome. The remaining 97.5% of their proteins are synthesized in the cytoplasm and are imported post-translationally and deposited into one of six plastidic compartments. This import and distribution of nuclear-encoded proteins into and within chloroplasts is a critical activity in plastid biosynthesis and homeostasis. While the nature of the energy requirements for the various chloroplast protein import machineries are known, the amount of energy utilized during protein transport and the parameters that mediate the energetics of these systems are generally not known.

Our work is directed toward quantitating the amount of energy used to transport proteins across chloroplast membranes and determining the source of that energy. With respect to the latter goal, we are investigating the location of protons that make up the localized proton pool long implicated in ATP synthesis and more recently, protein transport into the thylakoid lumen. To this end we are using targeted pH-dependent GFP to report the pH changes in the lumen in response to light.

FY 2012 HIGHLIGHTS

Plants transformed with pH-dependent GFP targeted to the thylakoid lumen do not display uniform fluorescence signals. Accordingly, we have used confocal microscopy to investigate the pH-responsive signal originating from individual chloroplasts in situ. These signals are sensitive to light, displaying fluorescence changes in the direction predicted by acidification of the lumen. We have further isolated one transformant that appears to display a stable GFP signal, and will use this plant as a source of chloroplasts for planned *in vitro* studies.

Investigations into Proteins Affecting Chloroplast Function

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Funding:	$145,000

PROGRAM SCOPE

The pfkB family of putative carbohydrate kinases is evolutionarily conserved and found in all kingdoms. Multiple members are found in all plants, yet the function of these proteins is not known in any plant species. We discovered that loss of function mutations in two closely related members, called *FLN1* and *FLN2*, have strong chloroplast defects in *Arabidopsis thaliana*, and the expression of a subset of chloroplast genes is strongly down-regulated in the mutants, indicating that these two proteins play and important role in chloroplast transcription and development. We propose to further understand FLN1 and FLN2 function. In addition, to help identify functions for other pfkB proteins, we propose to perform a bioinformatics analysis to identify conserved motifs, determine whether loss of function alleles for other pfkB proteins also have a phenotype, and determine where these other proteins localize within the cell.

FY2012 HIGHLIGHTS

We have made progress in the last year. Our initial studies on the *fln* mutants were published [J. Gilkerson, J. M. Perez-Ruiz, J. Chory, and J. Callis (2012)]. The plastid-localized pfkB-type carbohydrate kinases FRUCTOKINASE-LIKE 1 and 2 are essential for growth and development of *Arabidopsis thaliana* (BMC Plant Biology 12:102). This study suggested that FLN1 and FLN2 function together and are not functionally redundant. Graduate student John Riggs is exploring the possibility that the active form is a FLN1/FLN2 heteromer, and he has evidence to support this hypothesis. Using recombinant proteins, he showed that FLN1 and FLN2 preferentially form heteromers, rather than homomers. We are conducting additional interaction assays to see what affects interaction and are conducting activity assays to see if the heteromer has biochemical activity. Regarding the other 21 predicted pfkB proteins, we have conducted bioinformatic and literature searches. Twelve have unknown function and of those, two are under investigation in other labs. One unknown pfkB protein clades with bacterial ribokinases, and we will test whether this protein has ribokinase activity by complementation of the null bacterial strain.

For the others, we isolated T-DNA insertions in 8/10 uncharacterized pfkB genes. Some insertions are not nulls based on mRNA accumulation, and no phenotype is observed in single homozygous mutants, so we are obtaining additional alleles and crossing family members together. For localization studies, we are placing ORFs in plant expression vectors and will express them as fluorescent fusion tags for subcellular localization studies. We have very preliminary data that one ORF, At1g17160, localizes to a single punctum in each chloroplast—a slightly different pattern than for a known nucleoid-localized protein. We will determine the identity of these puncta. Altogether, these studies will greatly inform us regarding the role of this enigmatic protein family and define the role of both FLN proteins in chloroplast development and function.

Thylakoid Biogenesis – Significance of Protein Maturation and Mechanism of Protein Targeting

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PROGRAM SCOPE

The goal of this program is to define the mechanism underlying the development of photosynthetic membrane systems (thylakoids) in higher plant chloroplasts. To this end, we address several questions about an enzyme called plastidic type I signal peptidase (Plsp1). Plsp1 is vital for proper thylakoid development and seedling viability. It is located in the chloroplast envelope and thylakoid membranes, and is necessary for proper processing of the protein translocation channel Toc75 in the outer envelope and at least three photosynthetic proteins (PsbO, PsbP, and plastocyanin) in the thylakoid lumen. Distribution of Plsp1 in the two membranes coincides with the development of thylakoids from the envelope. Plastids that lack Plsp1 accumulate vesicles, which are believed to be thylakoid remnants as they contain the unprocessed intermediate form of PsbO (iPsbO) in peripheral areas.

The program uses biochemical and genetic tools to achieve the following three aims. The first aim is to test if accumulation of unprocessed lumenal proteins disrupts proper thylakoid development. The results should also provide mechanistic insights into the significance of signal peptide cleavage for protein function and assembly. The second aim is to test if a specific sequence dictates envelope localization of Plsp1 and to address the physiological importance of envelope-located Plsp1. The third aim is to test if Plsp1 interacts with other proteins in thylakoids by biochemical and live-cell imaging assays. Achieving these aims will enhance fundamental understanding of the dynamics of natural photosynthetic systems.

FY 2012 HIGHLIGHTS

The work about evolution of Plsp1 was published in November 2011 in *PLoS ONE*. For aim 1, we have used in vitro targeting assay to demonstrate that (i) “unprocessable” plastocyanin (due to amino acid substitutions around the Plsp1 processing site) is quickly degraded at thylakoids in light-dependent manner; (ii) unprocessable PsbO (iPsbO) forms a large oligomeric complex in the membrane; and (iii) iPsbP accumulates as a monomeric form in the membrane. Formation of the iPsbO-complex was also shown *in vivo* by using transgenic plants. These results are quite interesting because they indicate the presence of various mechanisms of protein quality control in thylakoids. We are currently defining underlying mechanisms of plastocyanin degradation, and are also identifying components of the iPsbO-complex. For aim 3, we demonstrated that Plsp1 forms a stable complex with PGRL1. PGRL1 is a protein that plays a role in regulation of PMF generation, possibly during the cyclic electron flow around PSI. Hence, its interaction with Plsp1 may indicate a connection between the photosynthetic electron flow and protein targeting, which depends on PMF. We are determined to define the significance of this interaction.

Multi-Frequency Pulsed EPR Studies of the Photosystem II Oxygen Evolving Complex

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Funding:	$180,000

PROGRAM SCOPE

The goal of this project is to develop electronic structure descriptions of the manganese/calcium cluster in photosystem II that is responsible for oxidizing water to molecular oxygen. In the process, the manganese cluster is oxidized by four electrons before it can direct O-O bond formation. Using our suite of magnetic resonance spectrometers, we characterize the magnetic structure of the Mn ions of this oxygen evolving complex (OEC) as well as its ligands (both proteinaceous and exogenous) at various stages of the catalytic cycle. To interpret these data, we utilize analogous results from studies of Mn-containing model compounds which have structural and/or spectroscopic similarities to the OEC. The latest generation of these models so closely mimic the structure of the OEC that there has been a renewed effort to make these inorganic molecules functional water oxidizers. Our spectroscopic findings on both the natural and synthetic systems will help to elucidate which structural features of the Mn cluster are requisite for catalysis.

FY 2012 HIGHLIGHTS

We have continued to fine-tune the picture we have of the OEC using results from our new, higher-frequency instrumentation. These spectrometers allowed us to characterize with high precision the nitrogenous ligands to the cluster. By monitoring changes in the degree of nitrogen coupling to Mn upon mutagenesis or chemical treatment with affecting small molecules, we have been able to evaluate proposals for the magnetic topology of the manganese cluster. Additionally, we have started to characterize a variety of synthetic complexes that, for the first time, model the asymmetric heterometallic core of the OEC. These complexes can be poised at many different levels of oxidation, thus mimicking the catalytic cycle. Further, the ligands can be varied systematically to see what effect such changes have on the spectral properties.

Photoreceptor Regulation and Optimization of Energy Harvesting in *Nostoc Punctiforme*

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Funding: $814,000

PROGRAM SCOPE

Sustainable sources of bioenergy production rely 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 one cyanobacterium, to improve our understanding of how they work, and to apply them in synthetic photosensory circuits for gene expression.

FY 2012 HIGHLIGHTS

Our consortium has successfully cloned, expressed, and purified all 41 photosensory domains of the bilin-based photosensors from *N. punctiforme,* a rainbow of sensors providing complete coverage of the entire visible spectrum and even the near-UV. In the past year, we have published basic descriptions of 30 of these proteins and an elucidation of the common mechanism used by many of these sensors to sense blue, violet, or UV light with an intrinsically red-absorbing bilin chromophore. We have also examined nine of these proteins using ultrafast spectroscopy, an undertaking which will allow us to examine conservation of photophysical mechanisms in these sensors, and have begun determination of atomic-resolution structures using NMR spectroscopy. In the next period, we look to continue these studies and to begin the construction of modular systems for light-regulated gene expression.

Membrane Bioenergetics of Halophilic Organisms

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Funding:	$185,000

PROGRAM SCOPE

This proposal is on the binding and functioning of carotenoid light-harvesting antennae to some recently-discovered microbial rhodopsins (xanthorhodopsin, gloeobacter rhodopsin and others). The study of xanthorhodopsin and the related dual-chromophore rhodopsins, such as gloeobacter rhodopsin reconstituted with salinixanthin or echinenone, represents an opportunity to explore the principles of excited-state energy transfer in a simple donor-acceptor system embedded in a protein. This will extend and compliment the knowledge gained in studies of carotenoid antennae in chlorophyll-based photosynthetic systems. Several intriguing unanswered questions will be addressed. *What are the structural requirements for energy transfer beyond binding of the carotenoid chain near the retinal and spectral overlap? What interactions fix the carotenoid 4-keto ring, conjugated chain, sugar moiety, and hydrocarbon chain in their respective binding sites? How modification of salinixanthin, the carotenoid antenna found in xanthorhodopsin, affects binding and energy transfer? What changes undergo carotenoid and retinal chromophores in the excited states upon photoexcitation and during the proton translocating photochemical cycle? Can the carotenoid serve as an internal sensor for the intramolecular events?* The carotenoid being near the retinal at a well-defined location provides a tool to monitor events in the retinal protein beginning from the excited states. Using light >550 nm for driving the retinal chromophore to the excited state, the changes in the absorption of the carotenoid from charge separation (due to the Stark effect, called also electrochromic effect) as well as the subsequent retinal isomerization during formation of J and K will be monitored in the fs to several ps time domain. The carotenoid changes will be followed also in the subsequent (dark stages) of the photocycle. We will explore the way changes are communicated from the retinal to the carotenoid during the dark reactions of the photocycle. *Finally, what other retinal proteins are capable of binding carotenoid and can antenna function be further enhanced by coupling with exogenous efficient light-harvesting systems such as quantum dots?*

FY 2012 HIGHLIGHTS

We were able to show (in collaboration with Prof Polivka) that photoexcitation of the retinal chromophore induces a large blue shift in the carotenoid absorption spectrum that decreases along with the decay of the retinal excited state. This provides evidence for a large change in the electrostatic field generated by the retinal excited state. A small shift remains in the first stable intermediate K and evolves during the photocycle along with other types which indicates loosening of carotenoid binding. We also show that there is an efficient energy transfer from quantum dots emitting at 480 nm and xanthorhodopsin, apparently from a coupling between the dots and salinixanthin. A new retinal protein potentially capable of carotenoid binding was examined.

Molecular Genetic Dissection of Chloroplast Iron Homeostasis

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Funding:	$175,000

PROGRAM SCOPE

Iron-deficiency is one of several abiotic stresses that impacts plant metabolism because of the loss of function of iron-containing enzymes in the chloroplast and mitochondria, including cytochromes, FeS proteins and FeSOD. In previous work, we distinguished four stages of iron nutrition—excess, replete, deficient and limited—based on phenotype and expression of sentinel genes. A profile of key iron-containing proteins of the chloroplast reveals a hierarchy of iron allocation to individual proteins depending on physiological demand for the pathways in which those proteins function. *How is this hierarchy determined?* Time course experiments allowed us to address this question. To discover new mechanisms of acclimation to poor iron nutrition, we surveyed the transcriptome of Chlamydomonas using RNA-Seq methodology. Presumed primary targets were identified in comparisons between visually asymptomatic iron-deficient vs. iron-replete cells. The output from the transcriptome was validated at multiple levels – by quantitative reverse transcriptase -PCR for assessing the data analysis pipeline, by quantitative proteomics for assessing the impact of changes in RNA abundance on the proteome, and by cross-species comparison for identifying conserved or universal response pathways.

FY 2012 HIGHLIGHTS

By studying the dynamics of acclimation to iron starvation, we showed the operation of two acclimation mechanisms in the iron-deficient chloroplast: an iron sparing pathway involving increased expression of an iron-independent MnSOD and an iron salvage and recycling pathway involving maintenance of FeSOD.

Comparative transcriptomics showed that more genes are impacted in photoheterotrophically grown cells compared to photoautotrophically grown ones with an overlap of only 24 between the two sets. The overlapping set represents key previously-described responses to poor iron nutrition, including most of the known components of high affinity iron uptake and some new candidates for distributive iron transport in Chlamydomonas. Whereas iron-deficiency illuminated the primary iron-specific response, a comparison of growth-inhibited iron-limited vs. –replete cells revealed significant changes in the expression of genes in chloroplastic oxidative stress response pathways among hundreds of other genes. We assessed the functional importance of three target genes, VTC2, MDAR1, and CGLD27, by biochemistry or reverse genetics. VTC2 and MDAR1, which are key enzymes in de novo ascorbate synthesis and ascorbate recycling via the ascorbate glutathione pathway, respectively, likely contribute to the ten-fold increase in ascorbate content of iron limited cells. CGLD27 is a highly conserved, presumed chloroplast-localized pioneer protein and is important for growth of Arabidopsis in low iron.

FTIR Studies of Photosynthetic Oxygen Production

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PROGRAM SCOPE

The oxidation of water to molecular oxygen is an extremely demanding chemical reaction, both thermodynamically and kinetically. The Mn_4Ca cluster in Photosystem II catalyzes this reaction far more efficiently than any synthetic catalyst. The reason for this efficiency is that the protein environment of the Mn_4Ca cluster controls the cluster's reactivity at each step in the catalytic cycle by choreographing the proton and electron transfer reactions associated with water oxidation and by managing both substrate (water) access and proton egress. Our goals are to identify and further delineate the dominant water access and proton egress pathways that link the Mn_4Ca cluster of with the thylakoid lumen and to identify the amino acid residues that serve as the critical bases that facilitate the oxidation of the Mn_4Ca cluster in its higher oxidation states. Our approach is to characterize mutant Photosystem II core complexes representing residues identified crystallographically or computationally as potentially participating in networks of hydrogen bonds or serving as catalytic bases. Our primary investigative tool is FTIR difference spectroscopy. Infrared spectroscopy is particularly suited for analyzing protonation/deprotonation reactions, pK_a shifts, and hydrogen bonded structures in proteins. Our recent work has focused on residues thought to participate in a dominant proton egress pathway leading from the Mn_4Ca cluster to the thylakoid lumen involving the Chloride ion (Cl^- 1) that is ligated by side chain amino group of D2-Lys317 and the backbone nitrogen of D1-Glu333.

FY 2012 HIGHLIGHTS

Our FTIR data show that the D2-K317R, D2-K317A, D2-K317Q, and D2-K317E mutations alter both polypeptide backbone conformation and carboxylate groups near the Mn_4Ca cluster. Our work, when combined with flash-induced O_2 yield measurements performed by Gary Brudvig and co-workers at Yale University, shows that the D2-K317A, D2-K317Q, and D2-K317E mutations decrease the efficiency of proton transfer from the Mn_4Ca cluster and destabilize the cluster's S_3 oxidation state.

Our FTIR data show that D1-Glu333 participates in the same network of hydrogen bonds that includes D1-Asp61, D1-Glu65, D2-Glu312, and D1-Glu329 and that extends at least 20 Å across the lumenal face of the Mn_4Ca cluster.

Preliminary time-resolved IR measurements conducted with R. Brian Dyer and colleagues at Emory University show that exogenous ferricyanide oxidizes the primary electron acceptor of photosystem II (Q_A^-) at a much faster rate than previously believed. We measured an instrumentation-limited half-time of 20 µs. This observation means that we should be able to measure Mn-oxidation-induced changes to backbone and carboxylate group conformations with resolution of 20 microseconds or better.

The Role of Auxin in Ambient Temperature Growth Regulation

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Funding:	$180,000

PROGRAM SCOPE

The sessile lifestyle of plants requires that they rapidly adapt to a constantly changing environment. Fluctuations in light and temperature, as well as water and nutrient availability, all require dynamic changes in growth and development. For crops and biofuel feedstocks, the way that the plant responds to the changing environment can have dramatic effects on yield. These issues are particularly pressing at a time when human activity is causing unprecedented changes in climate. Here we focus on the role of the plant hormone auxin in plant responses to changes in ambient temperature. This proposal is based on the discovery that auxin has a key role in the plant's response to changes in temperature within the normal growth range. In the Arabidopsis seedling, an increase in temperature results in a rapid and dramatic increase in organ elongation. In addition, we find that one of the auxin receptors, AFB4, has a particularly crucial role in this process. There are five specific aims. In the first, we will describe the characterize response of seedlings to elevated temperature with high temporal resolution, both with respect to growth and transcriptional changes. In the second aim, we will identify transcription factors that mediate this growth response and investigate the associated transcriptional networks. In the third aim, we will identify the factors responsible for changes in auxin level during temperature-regulated growth. In the fourth aim, we will perform genetic and biochemical experiments to investigate the function of the AFB4 and AFB5 proteins in auxin response and the temperature growth response. In the last aim, we will conduct a screen to identify new genes that function in temperature response

FY 2012 HIGHLIGHTS

We have focused our efforts in two areas. In the first, we performed a detailed analysis of the Arabidopsis seedling transcriptome during the early stages of temperature response. We find that approximately 200 genes respond within 10’ of temperature shift and a large fraction of these are auxin dependent. We are currently working on a more complete analysis of this data set in preparation for publication. In the second area of focus, we have directly investigated changes in auxin signaling in response to temperature. We find that levels of the auxin receptor TIR1 increase at elevated temperatures consistent with increased growth. Further, we show that an increase in TIR1 level is due to a decrease in TIR1 degradation and that this effect is mediated by the chaperone HSP90 and co-chaperone SGT1. In addition we find that HSP90 and SGT1 interact directly with SCF^{TIR1}. This is a novel and exciting finding that suggests HSP90 has a key role in the temperature-dependent growth response.

Biochemical Integration of Metabolic Networks Critical for Energy Transformation in *Chlamydomonas Reinhardtii*

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PROGRAM SCOPE

This project, initiated in August 2012, is focused on the photoautotrophic organism *Chlamydomonas reinhardtii* and the network of metabolic interactions that occur in the light and in the dark. Our goal is to understand the localization of biochemical pathways in compartments in the cell; examine key metabolic hubs present in chloroplasts, mitochondria, and the cytoplasm; and probe the ways that proteins associated with those hubs interact. The major metabolic junctures that we are focusing on include the hydrogenases (HYDA1/HYDA2), pyruvate-formate lyase and pyruvate-ferredoxin oxidoreductase (PFL1-PFR1), the transhydrogenase (NTH1), and alcohol dehydrogenase (ADH1).

FY 2012 HIGHLIGHTS

(1) One key hub in both respiratory and fermentation metabolism is the point at which pyruvate can be used as a substrate for a number of different enzymes. Two enzymes that represent critical routes for pyruvate metabolism under anoxic conditions are PFR1 and PFL1. We have worked extensively on PFL1 [Plant Cell. 24: 692-707 (2012)], but have only just begun to analyze PFR1 and its catalytic activity. We have five different mutant alleles of *PFR1* that were obtained by TILLING; a number of the alterations in the amino acid sequence of the mutants are non-conservative substitutions (e.g., E686K, E700K, K421N, M567I, P742S; the underlined changes are non-conservative substitutions).

(2) We have performed a significant amount of characterization of a transhydrogenase mutant (*nth1*). This mutant is unable to grow in the dark, potentially because it cannot make enough NADPH (mostly NADH is synthesized in the dark, and it would not be converted to NADPH in the mutant) to drive anabolic processes.

(3) A ferredoxin mutant (*fdx5*) recently examined is also unable to grow in the dark, and some very recent data suggests that it has aberrant lipid profiles. Additional analyses are required to more precisely define the changes in cellular lipids.

(4) Another critical hub involves the conversion of acetyl-CoA to either alcohol or acetate under hypoxic or anoxic conditions. A mutant in alcohol dehydrogenase was previously characterized [Plant Physiol. 158: 1293-1305 (2102)]. We now have mutants in the genes that encode proteins involved in the conversion of acetyl-CoA to acetate; these genes encode phosphate acetate kinase (PAT) and acetate kinase (ACK). There are two genes each that encode ACK and PAT. ACK1 appears to be localized in the chloroplast, ACK2 in the mitochondria, PAT1 in the mitochondria and PAT2 in the chloroplast. We have now inactivated three of these four genes and recently demonstrated that *ack1 ack2* double mutant has no acetate kinase activity (measured in cell extracts). However, interestingly, the mutant can still synthesize acetate in vivo, probably a consequence of genes encoding acetate synthase (ACS). The

generation and utilization of acetate and the metabolic factors critical for its synthesis are being explored.

Integration of Sugar Transport, Metabolism and Sensing in Arabidopsis: Optimizing Energy Efficiency in Plants- Evaluating and Targeting Leaks.

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Funding:	$190,000

PROGRAM SCOPE

Plants, through yet unknown mechanisms, sequester large quantities of reduced carbon into the soil. Carbon secretion amounts to a significant drain of the overall energy status of the plant, with an estimated 1.5 t ha^{-1} a^{-}1, or in other words, up to 30% of the net CO_2 assimilation. It has been speculated that secreted carbohydrates serve in attracting/feeding of beneficial microorganisms in the rhizosphere. Sugar secretion systems are also required as a crucial step in phloem loading, seed filling, and nectar section; in all cases, the underlying mechanisms were unknown. As a consequence, it has neither been possible to determine the exact location of efflux in any of the different plant organs, nor could the physiological role of sugar secretion be tested experimentally. Identification of these secretory systems will be necessary to engineer and optimize carbon budgets of crop plants and to ultimately increase productivity in agriculture and biofuels production. Our lab developed a novel set of tools that allows us to visualize and quantify sugar uptake and secretion, namely Förster Resonance Energy Transfer (FRET) nanosensors. In this project, we have deployed glucose and sucrose FRET sensors to identify and characterize the efflux carriers and to determine the effect of mutations in these transporters on the plant properties. The use of these FRET sensors in a mammalian expression system allowed us to identify a novel class of sugar effluxers that shares functional features with the transport activities detected using our FRET sensors in plant roots. The aim of this project is to identify and characterize sugar efflux transporters and to lay the basis for the construction of transgenic plants with altered efflux rates by overexpression and repression of the expression of the respective genes.

FY 2012 HIGHLIGHTS

We successfully identified a novel subclass of SWEET transporters for sucrose and demonstrated a key role in phloem loading [Science 335:207-211 (2012)]. We developed a screening system to analyze mutant plants [J Exp Bot 62:2411-2417 (2011)] as well as a microfluidic RootChip for monitoring FRET sensor responses with minimal invasion in roots [Plant Cell 23: in press (2011); Journal of Visualized Experiments : JoVE (2012)]. Importantly, we could show that SWEETs are key factors in plant pathogen interactions and mutation of SWEET genes leads to pathogen resistance [Nature 468:527-532 (2010)]. This novel class of sugar transporters has properties that match the ones we described in Arabidopsis roots [Plant J 56:948-962 (2008)]. We currently analyze SWEET family members that play roles in sugar secretion in roots and other plant organs important for carbon allocation and thus yield.

Studies of Structure and Dynamics of Light Harvesting Complex 1 of R. Sphaeroides by Solid State NMR

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PROGRAM SCOPE

We proposed to characterize the structure and conformational dynamics of light harvesting complex I of *Rb. sphaeroides*, the immediate antenna complex serving the photosynthetic reaction center. We propose to elucidate the structure, function, and dynamics using solid-state NMR studies of the intact complex. In contrast to the photosynthetic reaction center, and the more remote light harvesting complex 2, light harvesting complex 1 has not been characterized at high resolution, although a 4.8 A resolution structure has been determined. Our preliminary signal assignments for both protein and chromophores in the complex indicate the feasibility of molecular level studies of this system by solid state NMR, including structure and dynamic characterization.

FY 2012 HIGHLIGHTS

We discovered a potentially important conformational flexibility in LH1, namely the torsional angle in the exocyclic acetyl group of the BChl pigments. This conformational degree of freedom has been indicated previously as potentially powerful for tuning the optical properties of the key chromophores of the light harvesting system; but its plasticity has not been studied experimentally previously, and NMR data allow this study.

During this year, we established and tested methods for dynamic characterization, namely the sub-ns conformational dynamics of the chromophores and nearly protein functional groups in the protein. Our recent manuscript describes a new method using ^{2}H or deuterium NMR of extensively isotopically triply enriched (^{15}N, ^{13}C, ^{2}H) proteins to obtain order parameters describing the extent of fast limit librational motion; the deuterium dimension in a multidimensional experiment can yield an order parameter. The methods have been applied to model systems and to a small protein, and cross-validated against other spectroscopic strategies to obtain order parameters; the advantage of multiple probes is that a more detailed model of the motions can be developed. We are now utilizing these methods on LH1 to measure the dynamical disorder as a function of temperature.

To determine the three dimensional structure of the complex, it is essential to have the protein NMR resonances as well dispersed as possible. Our spectra from Rhodobacter spheroids are very congested, and we are assessing spectra from other Rhodobacter.

Chloroplast Dynamics and Photosynthetic Efficiency

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PROGRAM SCOPE

We propose to investigate 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 light that can cause photodamage. Plastids sometimes extend their reach by sending out projections (stromules) that can connect anchor chloroplasts in position within the cell or provide close contact with the 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, although the actin cytoskeleton is known to be critical. The receptors responsible for detection of light level have been identified, but how the signals ultimately result in chloroplast localization is not understood. We propose to examine 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. Intracellular location of myosin XIs and myosin-interacting proteins and the dynamics of the actin cytoskeleton in wild-type, mutants, and silenced plants will be examined by microscopy of fluorescent fusion proteins under different light regimens. 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 C4 photosynthesis into C3 plants as well as to engineer improved photosynthetic efficiency in C3 plants.

FY 2012 HIGHLIGHTS

Using an optimized chloroplast movement monitoring system, we have observed a role of myosin XIs in chloroplast movement by silencing multiple genes simultaneously. We have also been able to observe dominant negative effects of expression of defective myosins on Golgi and mitochondrial movement. We have identified some new factors affecting chloroplast movement through a proteomics screen followed by transient silencing.

Studies on Cytochrome bo3 from Escherichia Coli

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PROGRAM SCOPE

Cytochrome bo_3 from *E. coli* is a respiratory oxygen reductase and a member of the heme-copper oxidase superfamily. This enzyme uses ubiquinol as an electron source, and e is a proton pump, coupling the redox chemistry of the reduction of O_2 (to water) to the generation of a transmembrane voltage (proton motive force). Our goal is to understand how Nature has solved the problem of efficiently converting chemical energy into electrical energy. We are addressing several related questions: (1) How does the protein modulate the properties of the bound quinone substrate? (2) What are the protonation states of key residues in different redox states of the enzyme? (3) How does oxygen diffuse through the protein to get to the active site? (4) How do internal charge movements alter the internal electric field within the enzyme? (5) What is the structure of the enzyme, and how does it change in intermediate states during catalysis?

FY 2012 HIGHLIGHTS

Work has focused on the question of how the protein modulates the properties of the bound quinone. The enzyme contains a non-covalently bound ubiquinone-8, which acts as a cofactor during catalysis. It is thought that this bound quinone becomes reduced by 2-electrons and then delivers the electrons, one at a time, to the heme b redox component. Hence, the bound quinone transiently exists in the one-electron reduced semiquinone state (ubiSQ). This is paramagnetic and provides an opportunity to use EPR spectroscopy to decipher the nature of the interactions with residues in the protein binding site. We have made excellent progress working with Dr. Sergei Dikanov (Univ of IL) using two-dimensional pulsed EPR techniques, and to assist in this work, we have constructed a series of variants of the enzyme that are selectively labeled with ^{13}C, ^{15}N, or ^{2}H stable isotopes in amino acid residues and in the ubiquinone.

By labeling the methyl and methoxy ring substituents of the ubiSQ with ^{13}C, we measured the hyperfine interactions coupling the nuclear spin with the electron spin of the ubiSQ, providing information about the distribution of unpaired spin in the ubiSQ. The data indicated that the protein constrains the conformation of the methoxy groups. This is significant because the conformations of these groups influence the extent of electron withdrawal from the π system of the ubiSQ ring and, therefore, the electrochemical properties of the ubiSQ. In addition, we characterized a mutant, D75H, which also stabilizes the ubiSQ but is catalytically inactive. We found that the newly introduced histidine makes a strong hydrogen bond with the ubiSQ while, at the same time, the strong hydrogen bond with arginine-71 that is present in the wild type enzyme is absent from the inactive mutant.

Regulation of Chloroplast Biogenesis: the *Immutans* Mutant of Arabidopsis

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PROGRAM SCOPE

The goal of this project is to gain insight into mechanisms of chloroplast biogenesis using the *immutans* variegation mutant of Arabidopsis as a model system. Sectoring in *immutans* is light-sensitive and caused by a nuclear recessive mutation. Cells in the green sectors of the mutant contain morphologically-normal chloroplasts, whereas cells in the white sectors have abnormal plastids that lack organized lamellae. The *immutans* gene product was originally identified as a plastoquinol terminal oxidase (PTOX) on the basis of limited homology to alternative oxidase (AOX), a quinol terminal oxidase in the alternative pathway of respiration in mitochondrial inner membranes. This assignment has since been verified and the enzymatic properties of PTOX have been extensively studied. PTOX has also been found to participate in a growing number of metabolic pathways in plastids, including the desaturation reactions of carotenoid biosynthesis and chlororespiration. It also serves as a stress safety valve during photosynthetic electron transport and participates in the control of cyclic electron flow around PSI. The fact that all *immutans* cells have a uniform genotype raises the question of how morphologically-normal green tissues arise in the mutant plants. To address this question, we have generated and characterized second-site genetic suppressors of *im* that give rise to all-green plants. It is presumed that such suppressors define activities/processes that substitute for or bypass the need for PTOX. Hence, these mutants provide a unique opportunity to gain insight into mechanisms of PTOX action, alternative electron sink function during photosynthetic electron transport, and chloroplast biogenesis.

FY 2012 HIGHLIGHTS

To date, seven *immutans* suppressor lines have been isolated; and these lines are in various stages of molecular characterization. During the past year, we have completed molecular analyses of an activation-tagged suppressor line (designated *ATG791*) in which *im* is rescued by overexpression of AOX2, thought to reside exclusively in mitochondria. However, we found that AOX2 is present in thylakoids of the tagged lines, where it is able to replace PTOX activity. Chloroplast AOX2 is found in high molecular weight complexes in thylakoids, and its presence does not disturb steady state photosynthesis. Because AOX2 was targeted to plastids using its own localization sequences, we hypothesize that it is a dual-targeted protein (plastids and mitochondria), and speculate that it functions to supplement PTOX activity during the early events of chloroplast biogenesis. We further propose that chloroplast AOX2 might define novel electron transport pathways. The ability of AOX2 to substitute for PTOX in the correct physiological and developmental contexts is a striking example of the capacity of a mitochondrial protein to replace the function of a chloroplast protein, and illustrates the plasticity of the photosynthetic apparatus.

Structure/Function of the Novel Proteins LCIB and LCIC in the Chlamydomonas CCM

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Funding:	$170,000

PROGRAM SCOPE

The goal of this project is to investigate the function of a novel protein, LCIB, which is an essential component of the CO_2-concentrating mechanism (CCM) required by microalgae to grow in environments where inorganic carbon (Ci, CO_2, and HCO_3^-) levels are at or below air equilibration levels of CO_2 (~0.038%). Microalgae together with cyanobacteria are responsible for approximately half of the earth's primary photosynthetic productivity, but our understanding of the functional components and the detailed mechanisms comprising the microalgal CCMs still is limited. Identification in *Chlamydomonas reinhardtii* (Chlamydomonas) of essential CCM components, including LCIB, have 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.

We hypothesize that LCIB and the very similar protein, LCIC, combine to form a multimeric complex that traps stromal CO_2 and converts it vectorially into stromal HCO_3^-. This vectorial conversion of CO_2 into HCO_3^- not only could prevent loss of stromal CO_2 released by dehydration of HCO_3^- in the thylakoid lumen, but also may capture external CO_2 diffusing into the stroma by trapping it as HCO_3^-. The experimental plan of this proposal will test this hypothesis based on the following specific aims: (1) Investigate the function of LCIB, LCIC, and the LCIB/LCIC complex in the microalgal CCM using a combination of reverse and forward genetics. (2) Investigate the structure/function of LCIB/LCIC complexes both *in vivo* and *in vitro*. (3) Determine the structure of LCIB, LCIC, and the LCIB/LCIC complex.

Resonant and Non-Resonant Hole-Burning and Delta Fluorescence Line-Narrowing Studies of BChls in Excitonically Coupled Photosynthetic Systems

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PROGRAM SCOPE

This project focuses on excitonically coupled bacteriochlorophylls (BChls) that are ubiquitous in bacterial photosynthetic complexes. Hole-burning (HB) and delta fluorescence line-narrowing (ΔFLNS) spectroscopies and modeling studies (using Redfield theory) are used to provide additional insight into the excitonic structure, electron-phonon and vibronic couplings, ligation of pigments, and excitation energy transfer (EET)/electron transfer (ET) processes in (1) various model protein systems (with a variable number of BChls); (2) the Zn-reaction center (RC) from *Rb. Sphaeroides* (Zn-RC with six Zn-BChls) and its mutants; and (3) various FMO antenna protein complexes (with 7 and 8 BChls per monomer), found in anoxygenic green sulfur photosynthetic bacteria. Comparative studies of relatively simple functional models of BChls in the protein environment serve as a strategy for better understanding the roles of specific elements within more complex natural photosynthetic systems. One of the goals is to better understand the experimentally observed holes and anti-holes in Zn-BChls monomers, excitonically coupled Zn-BChls dimers, tetramers, and multichromophoric BChls systems. Deeper insight into the origin of hole-burned spectra (both resonant and nonresonant) in excitonically coupled systems will provide a better framework for probing the electronic structure of complex biological systems via HB spectroscopy. Our methodologies and excitonic calculations should provide a more complete picture of the EET processes in various photosynthetic antennas and ET in various mutants of bacterial RCs.

FY 2012 HIGHLIGHTS

We have developed programs to model various optical spectra including resonant and nonresonant hole-burned spectra (using Redfield theory) obtained for multichromophoric systems. Four manuscripts have been published; for example, we have provided new insight into ET in *Rhodobacter sphaeroides* RC containing Zn-BChls and ET pathways in isolated Photosystem II RC from *Chlamydomonas reinhardtii.* (See, for example, the invited Perspective in *J. Phys. Chem. Lett*. (2012) 3, 1684-1694). Preliminary data, including various hole-burned spectra, were already obtained for various FMO and water soluble binding proteins from the *L. virginicum* and *cauliflower*, and modeling studies of various optical spectra continue. In the next period we will demonstrate that, contrary to the presently accepted consensus, the 825 nm band in the FMO complex cannot be explained by a single transition. Preliminary data clearly suggest that downward uncorrelated energy transfer between trimer subunits must be taken into account in order to explain the shape of emission and HB spectra.

Photosystem II: Structure and Assembly

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PROGRAM SCOPE

Elucidation of the functional properties, structural organization, and assembly of membrane protein complexes is one of the central objectives of current biochemical investigation. In our laboratory, we focus on Photosystem II (PS II). While much progress has been made in the understanding of these processes in the photosystem, the structural interactions of a number of extrinsic subunits in both higher plants and cyanobacteria with the intrinsic components of PS II remain elusive. Additionally, the molecular pathways delivering water to the active site of PS II and removing molecular oxygen and possibly reactive oxygen species (ROS) from the active site have not been determined. The locations of ROS production on the reducing side of the photosystem have also not been unequivocally identified. Finally, the mechanisms involved in the assembly and repair of the photosystem remain poorly understood. A combination of biochemical, biophysical, and molecular approaches is being used in our studies.

FY 2012 HIGHLIGHTS

(1) In *Synechocystis* we have determined that CP43:^{320}R (equivalent of CP43:^{321}R in *T. vulcans*) is required for the binding of both PsbV and PsbU to the photosystem. This confirmed a prediction that we had earlier made based on the *T. vulcans* crystal structure. Additionally, the N-terminal cystinyl residue (^{22}C before processing) of CyanoQ, which normally contains a lipid modification, is required for the stable assembly of this subunit into the photosystem.

(2) In higher plant PS II, we have determined that ROS produced on the oxidizing side of the photosystem can modify CP43: ^{354}E, ^{355}T, ^{356}M, and ^{357}R. These residues are in close proximity to the Mn_4O_5Ca cluster and appear to lie on a pathway vectoring ROS and possibly molecular oxygen away from the metal cluster. On the reducing side of the photosystem, we have identified oxidized residues in close proximity to both Q_A (D1:^{239}F, ^{241}Q, ^{242}E and D2:^{238}P, ^{239}T, ^{242}E, and ^{247}M) and Pheo$_{D1}$ (D1:^{130}E, ^{133}L, and ^{135}F). These findings strongly suggest that both of these redox cofactors can produce ROS.

(3) We have determined that the Sll0606 protein, which is required for PS II assembly in *Synechocystis*, is an intrinsic membrane protein component.

(4) We have been examining the haploid model organism *Physcomitrella patens* for possible use in some of these studies. Importantly, we have isolated a novel strain of this moss that can grow photoheterotrophically on sucrose in the presence of DCMU. This strain may be very useful in a variety of studies examining PS II structure, function, and assembly.

Early Career: Tha4 Topology and Direct Interaction with Translocating Precursor Mature Domain During Transport on the cpTat Pathway

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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 2012 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. One of the three transmembrane cpTat components, Tha4, is thought to function as the pore by forming an oligomer. Yet, little is known about the basic topology of Tha4 in thylakoid and little work has been done to detect precursor-Tha4 interactions, which are expected if Tha4 is the pore. First, we completed topology studies of Tha4 via cysteine accessibility to membrane permeant and impermeant labels. These data support a N_{out}-C_{in} topology for Tha4 in the thylakoid membranes. Second, we have the first evidence of interaction of the mature domain of precursor with Tha4. Using disulfide exchange, we demonstrate that the mature domain of the precursor interacts specifically with the amphipathic helix of Tha4, suggesting a role for Tha4 as the precursor conduit. These data provide the first evidence that Tha4 participates directly in transport of precursor on the cpTat pathway. [J Biol Chem 287: 34752–34763 (2012), Plant Physiology (2012)]

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

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 from 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.

FY 2012 HIGHLIGHTS

Genetically engineered plants with specific alterations in end product synthesis were studied. These plants lack daytime sucrose production (tpt plants) or daytime leaf starch synthesis (pgm plants). These plants were measured at 15, 25, and 35°C over a range of carbon dioxide from zero to 1000 ppm. These plants showed that at low rates of photosynthesis, the altered genetic makeup had little effect on photosynthetic rate. Starch and sucrose synthesis showed little compensation; plants that could not make sucrose during the day made very little extra starch to compensate. Starch and sucrose synthesis were more strongly temperature-dependent than either the light reactions or the carbon dioxide fixing enzyme (Rubisco). At low temperature, starch and sucrose synthesis often limited the overall rate of photosynthesis, while at high temperature, only when either starch or sucrose synthesis was blocked, was photosynthesis limited. Photosynthetic limitation by end product synthesis was evident in loss of oxygen sensitivity and increased resistance to ATP formation (increased proton motive force). These experiments have been completed with Arabidopsis plants and will now be repeated with tobacco plants. Because tobacco has much higher rates of photosynthesis, regulation may be more crucial.

We have begun designing genes to test the role of hexose phosphate in the overall regulation of photosynthesis by end products. These plants should be ready by next year.

Mechanisms of Chloroplast Division in Plants

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PROGRAM SCOPE

The division of chloroplasts by binary fission is essential for maximizing the efficiency of light harvesting and CO_2 fixation in plants. Chloroplast division is orchestrated by a macromolecular machine comprising sub-complexes localized both inside and outside the organelle, whose individual components must be properly assembled at the division site and their activities coordinated across the two envelope membranes to constrict and sever the organelle. The overall focus of the currently funded project is functional analysis of two key components of the chloroplast division complex, ARC6 and its paralog PARC6. These proteins both reside in the inner envelope membrane and function together in part to regulate assembly of the stromal FtsZ ring (Z ring) and in part to coordinate the positioning and contractile activities of the internal Z ring and external dynamin ring across the two envelope membranes. Our long-term goal is to fully elucidate the biochemical, molecular, and regulatory processes controlling chloroplast division in plants.

FY 2012 HIGHLIGHTS

Arabidopsis PARC6 was predicted to have two transmembrane domains, but some orthologous proteins from other plants were predicted to have one. We designed and tested several PARC6 constructs by deleting one or both predicted transmembrane domains and determining whether the resulting proteins were membrane-associated. The results demonstrated that PARC6 only has a single transmembrane domain, leading to the conclusion that PARC6 spans the inner envelope membrane with its amino-terminus facing the stroma and its C-terminus protruding into the intermembrane space (IMS). Based on the new topology, we retested interactions between PARC6 and several other chloroplast division proteins. We detected a new positive interaction between the IMS regions of PARC6 and the outer envelope protein PDV1. We further found that a PDV1 mutation shown previously to interfere with chloroplast division *in vivo* also inhibited PARC6-PDV1 interaction, suggesting that the division defect in PDV1 is due to the reduced interaction. These and other findings suggest that direct interaction between PARC6 and PDV1 positions PDV1 at the chloroplast division site.

Previously, we showed that a portion of the stromal region of PARC6 interacts with the chloroplast division protein ARC3, and that both proteins negatively regulate Z-ring assembly to ensure proper Z-ring positioning at the mid-plastid division site. Although ARC3 was reported by another group to interact uniquely with FtsZ1, we discovered that ARC3 also interacts with and regulates assembly of FtsZ2. Recent genetic analysis has shown that PARC6 and ARC3 also have distinct functions in the chloroplast division complex and in division-site positioning. Together, these and related findings are leading to new hypotheses concerning how the chloroplast division complex is assembled and how division-site positioning is controlled.

Regulation of Thylakoid Lipid Biosynthesis in Plants

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Funding:	$190,000

PROGRAM SCOPE

Chloroplasts with their intricate photosynthetic membranes provide the basis of biomass production by plants. They enable plants to convert sunlight into chemical energy, to fix carbon dioxide and to produce oxygen. An improved mechanistic understanding of the development and function of chloroplasts is sought. Focus is on the assembly of the lipid components of the photosynthetic membrane, in particular on the galactoglycerolipids as the predominant lipids in this membrane. Galactosyltransferases associated with the inner and outer chloroplast envelope membranes assemble the bulk of galactoglycerolipids from UDP-galactose and diacylglycerol. The diacylglycerol moiety can be assembled at the endoplasmic reticulum (ER) or at the inner chloroplast envelope membrane. As a consequence, precursors for a substantial amount of galactolipids must be imported into the plastid. Mutants of Arabidopsis disrupted in the import of lipids from the ER accumulate unusual oligogalactolipids and triacylglycerols. Oligogalactolipid synthesis has also been observed in isolated chloroplasts, and was attributed to the activation of a processive galactolipid:galactolipid galactosyltransferase associated with the chloroplast outer envelope. The gene encoding this activity was identified as SENSITIVE TO FREEZING 2 and is ubiquitous in plants. The goals are to provide an understanding of SFR2 function in chloroplast biogenesis and maintenance, its biochemical properties, and its regulation of activity, and in the long term to explore its utility for plant protection. Specific objectives are to (1) study SFR2 function in its physiological context, (2) understand the role of SFR2 activation in lipid trafficking mutants, (3) determine the biochemical mechanism of SFR2 activation, and (4) probe diacylglycerol (DAG) pools, as they are affected by the activity of SFR2. It is proposed that SFR2 is involved in chloroplast lipid remodeling, thereby protecting plants from diverse abiotic stresses that can severely impact crop yield.

FY 2012 HIGHLIGHTS

The region of SFR2 that selects for hydrophobic lipid substrates was identified using a model of the protein to inform site-directed mutagenesis. Specific antibodies against the N- and C-termini of SFR2 were produced and purified, and are being used to study SFR2 topology. A new assay, which directly tests activation of SFR2 *in organello* using isolated chloroplasts from different plant species, was developed.

Transgenic plants targeting *E. coli* diacylglycerol kinase to different membranes were characterized. The localization of recombinant DAG kinases targeted to different chloroplast membranes was confirmed. Specific changes in subcellular lipid pools were observed in the absence and presence of SFR2 activity, providing proof-of-concept for an *in vivo* synthetic biology approach towards manipulating and probing subcellular lipid pools in plants.

The Energy Budget of Steady State Photosynthesis

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Funding:	$230,000

PROGRAM SCOPE

Photosynthesis is the richest source of energy for life on our planet, but it can also generate highly reactive chemical species that can kill the organisms it powers. Photosynthesis must therefore be finely regulated to balance the competing needs for efficient energy conversion and the avoidance of deleterious side reactions. The project goals focus on understanding how photosynthesis balances its energy budget, matching the output of energy in NADPH and ATP to precisely meet biochemical demands. If this balancing does not occur, the system will fail, leading to photodamage and loss of energy storage. Efforts to improve the efficiency of photosynthesis by introducing CO_2 concentrating mechanisms, altering metabolism, or biosynthetic pathways to shunt energy to alternative products, will likely exacerbate these imbalances. Our specific aims concern the mechanisms of (1) cyclic electron flow (CEF) which acts to generate ATP to balance the chloroplast energy budget, and (2) the transport and sharing of ATP among the chloroplast, cytoplasm, and mitochondria.

FY 2012 HIGHLIGHTS

Loss of coordinated protein expression in the plastid leads to partially assembled photosynthetic complexes, generation of reactive oxygen, and activation of cyclic electron flow (CEF) – We isolated several new mutants of Arabidopsis plants with elevated CEF. One of these, hcef2, was mapped to TADA1, a chloroplast tRNA editing enzyme. We show evidence that loss of TADA1 results in uncoordinated protein expression in the chloroplast, leading to partial assembly of chloroplast's energy transducing complexes (photosystem I and II, cytochrome b6f complex, ATP synthase, etc.). These mutants show high levels of H_2O_2 production, suggesting that partially assembled photosynthetic complexes can be toxic. We propose that H_2O_2 production activates CEF, supporting a new redox mechanism for its regulation.

A new redox switch for regulating CEF – We have also identified a new redox switch that governs the activity of CEF. Thylakoids isolated in the absence of reductants lose CEF activity. Activity is preserved upon isolation in a range of antioxidants, most notably dithiothreitol, suggesting that thioredoxin may be a regulator of CEF.

Rapid translocation of ATP across the chloroplast envelope: consequences for the energy budget of photosynthesis – Our experiments to measure CEF in intact chloroplasts led us to the striking and serendipitous finding that intact chloroplast preparations were capable of rapid export of ATP. A highly active chloroplast ATP exchange system *in vivo* would dramatically alter our views on photosynthetic metabolism, allowing greater flexibility in the photosynthetic and cellular energy budgets and allowing metabolic engineers to power new ATP, requiring metabolic pathways into plant cells.

MSH1: A Novel Inter-Organellar Environmental Response Mechanism in Higher Plants

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PROGRAM SCOPE

MSH1 is a plant-specific protein encoded in the nucleus but functioning in both mitochondria and chloroplasts. The protein carries out DNA recombination surveillance functions in both organelles and localizes to the nucleoid. However, the protein also influences organellar-nuclear retrograde signaling, resulting in profound changes in plant development with MSH1 depletion. The goals of the project are to (1) localize the MSH1 protein within the chloroplast, (2) identify its protein interactors within the organelle, and (3) characterize active sites within the protein that account for its multi-functionality. In addition, we have assessed epigenetic changes within the plant that occur in response to MSH1 disruption or down-regulation. The system we are studying is distinctly suited to the study of environmental stress sensing in plants, the underlying basis of crop growth vigor, and epigenetic variation in crop species amenable to manipulation to enhance crop performance.

FY 2012 HIGHLIGHTS

Our laboratory has made the following important advancements in our understanding of MSH1 behavior in plants. We have shown the following:

(1) Plants undergo a process of developmental reprogramming when MSH1 is mutated or down-regulated. These changes in development occur nearly identically in six different plant species tested, both monocot and dicot, and the changes are effected by signals from the chloroplast. The developmental reprogramming phenomenon is subsequently an epigenetic state that is stably inherited independent of the RNAi transgene. These observations are published in *Plant Physiology*.

(2) Crossing plants that have undergone developmental reprogramming with their original, unaltered, and isogenic wildtype counterparts produces a condition of enhanced growth and displays striking levels of phenotypic non-genetic variation. We postulate these changes to be the consequence of epigenetic variation that emerges with MSH1 down-regulation and chloroplast signaling. These observations likely comprise natural plant epigenetic changes in response to environmental stress, and provide the first opportunity to conduct epigenetic manipulation as a crop breeding strategy. This variation has been observed in sorghum, Arabidopsis, soybean, tobacco, tomato, and millet. Results from Arabidopsis and sorghum are presented in a manuscript that has been submitted for publication.

(3) MSH1 localizes to the chloroplast thylakoid membrane, and interacts with components of the photosystem II oxygen evolving complex (PsbO1/PsbO2, PPD3, and D1) and a component of the cytochrome B6F complex (PetC). Consequently, we hypothesize that MSH1 anchors to the thylakoid membrane and resides between the PSII-OEC and Cyt B6F near plastoquinone. MSH1 is predominantly within specialized sensory plastids of epidermal and bundle sheath/xylem parenchyma cells, with little or no MSH1 protein observed in mesophyll plastids. These observations suggest that MSH1 participates in a specialized signaling process unique to plants.

Role of the Rubisco Small Subunit

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PROGRAM SCOPE

Ribulose-1,5-bisphosphate carboxylase/oxygenase (Rubisco) is the most abundant protein on earth, and catalyzes the rate-limiting step of photosynthetic CO_2 fixation. Because the enzyme is competitively inhibited by O_2, there is much interest in engineering Rubisco to increase the rate of CO_2 fixation or decrease O_2 inhibition. An increase in net CO_2 fixation would lead to an increase in the production of food and biomass for renewable energy. However, it has been 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. In contrast, all of these gene copies have been eliminated in the green alga *Chlamydomonas reinhardtii*, which is presently the only eukaryotic 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 potential means for ultimately improving Rubisco. Research has focused on the loop between β-strands A and B, which is the most variable structural feature of the Rubisco small subunit. The βA-βB 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. Directed mutagenesis and transformation have shown that residue substitutions or insertions in the small-subunit loop can influence large-subunit catalysis and CO_2/O_2 specificity even though the loop is far from the active site and holoenzyme structural transitions remain normal. Ala-scanning mutagenesis of the most-conserved small-subunit residues has also identified other regions of interaction between large and small subunits that affect catalysis and specificity. It appears that small subunits contribute to active-site structure by influencing the position of α-helix 8 in the large-subunit α/β barrel. Hybrid enzymes have been created comprised of plant small subunits and *Chlamydomonas* large subunits; and these enzymes have increases in CO_2/O_2 specificity, further indicating that small subunits may be the key for ultimately engineering an improved Rubisco enzyme.

FY 2012 HIGHLIGHTS

Several specific regions of interaction between large and small subunits have now been defined that influence Rubisco catalysis and CO_2/O_2 specificity. In the next phase of the project, these regions will be the focus of protein design and evolution *in vitro* aimed at improving Rubisco function. Because α helixes at the surface of the small subunit have recently been shown to be responsible for targeting Rubisco to the algal pyrenoid, which provides a system for concentrating CO_2 around Rubisco, further definition of the structural basis for targeting may provide insight into ways of increasing algal CO_2 fixation. Enhancements of algal growth may be useful for the production of biofuels.

Maximizing Photosystem II Water Oxidizing Efficiency Through the Identification of Optimal Protein Coordination Environments

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Funding:	$165,000

PROGRAM SCOPE

This project seeks to reveal the range of catalytic activities of water oxidizing complexes from a phylogenetically diverse range of oxygenic phototrophs. The photosynthetic enzyme that catalyzes water oxidation/oxygen evolution offers an ideal blueprint from which to learn lessons on how to design more efficient water splitting catalysts that are needed for developing next generation (renewable) solar fuels. We are conducting a systematic survey of catalytic water oxidation activities using both intact (native) cells and transgenic cells comprised of variants of the main protein scaffold that binds the catalytic core of the Photosystem II water-oxidizing complex (PSII-WOC). Our approach seeks to reveal the catalytic determinants of natural photosynthetic water oxidizing enzymes by examining the "desirable design motifs" among PSII-WOC enzymes having different protein scaffolds that deviate from native amino acid sequences. We utilize genetic tools for the introduction of non-native PSII protein sequences and specialized instrumentation for precision measurements of kinetic turnover (both charge separation and O_2 production).

This collaborative effort combines the expertise of Prof. G. Charles Dismukes and Research Prof. Gennady Ananyev (Rutgers) in biophysical chemistry and instrumentation with the experience of Prof. Susan Golden (UCSD) in cyanobacterial regulation of PSII protein components and Prof. Steven Mayfield (UCSD) in the genetic alteration of green algae.

FY2012 HIGHLIGHTS

We have engineered a green alga that grows to greater biomass yield at low light intensity. Either one of two native isoforms of the cyanobacterial D1 subunit were expressed in a *Chlamydomonas* background lacking its native D1. These two D1 isoforms are differentially expressed in cyanobacteria under low light and high light conditions, respectively, but evidence for a phenotypic advantage was previously lacking. This work provides the first evidence to our knowledge of a competitive growth advantage at low light intensity of cells expressing the D1:1 (low-light induced) isoform. We identified the molecular origin of this effect as a longer lifetime of PSII charge separation (slower charge recombination for D1:1 at low-light intensity). This work has been submitted to *Journal of Biological Chemistry.*

In the previous year, we also published a key paper identifying the oxidation states of the Mn atoms in the PSII-WOC using photo-assembly, thereby providing an alternative approach to XAS and ENDOR techniques [Kolling et al. *Biophys. J.*, *103*, 313-322 (2012)]. Our interpretation of the Mn oxidation states has sparked debate and provided new insights into the chemical principles essential for photosynthetic water oxidation. These principles are discussed in context through a submitted review article on PSII structure and function to *Annual Review of Biochemistry*.

Asparagine Synthetase Gene Regulatory Networks and Plant Nitrogen Metabolism

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Funding:	$170,000

PROGRAM SCOPE

The goal of this project is to model and alter gene regulatory networks affecting nitrogen (N) assimilation into asparagine (Asn), a C- and N-efficient amino acid used to transport and store nitrogen in seeds. Altering transcription of ASN1, the major gene controlling Asn synthesis in Arabidopsis, effects increases in seed-N, and this technology is in field trials of corn and other crops. Using a combined genetic, genomic, and systems biology approach, we have uncovered components regulating Asn synthesis and metabolism in response to carbon (C), light (L), and nitrogen (N) signals. In a positive genetic selection, a mutant (CLI186) was shown to impair the C and L repression of ASN1. CLI186 mutant was caused by the deletion of a histone methyltransferase, which plays an important role in the epigenetic control of genes involved in development and response to environment. Our goal is to explore the epigenetic and transcriptional control of ASN1 and N-assimilation in response to nutritional and environmental stimuli, with a combination of epigenomic, transcriptomic, and metabolic approaches. Combining epigenomic and transcriptomic data, we uncovered that CLI186 targets ~1,000 genes for H3K36m3 modification, to integrate biotic and abiotic stimuli to regulate genes involved in development and metabolism. This analysis identified several transcription factors (TFs) predicted to regulate ASN1 as targets of H3K36me3 methylation by CLI186. In addition, our gene regulatory networks predict that these TFs potentially reciprocally regulate Asn synthesis (via ASN1) and degradation (via ANS1). Currently those TFs are being tested with knockout mutants and overexpressors, as well as using a transient inducible overexpression system, to verify their role in the ASN1-metabolic regulatory network**.** We also aim to integrate our studies on transcriptional control of N-assimilation into Asn into a regulatory network model that encompasses changes in N-metabolites. We have thus begun measuring changes in temporal levels of the primary N-assimilation products (Glu, Gln, Asp, Asn) using ^{15}N labeling, in WT and mutants in Asn metabolism genes, and in putative regulatory TFs. The combined epigenetic, transcriptional, and metabolic analyses will let us determine whether and how perturbations in N-assimilation gene network affect endogenous Asn.

FY 2012 HIGHLIGHTS

The genome-wide CLI186-mediated epigenetic and transcriptional control in response to L and C was profiled by ChIP-SEQ and microarrays in wild-type and cli186 mutants. We observed a dramatic decrease in H3K36me3 levels for ~4,000 genes, accompanied by a reduction in gene expression levels. Combining the epigenomic and transcriptomic data, we identified ~1,000 genes as potential direct targets of histone modification by CLI186, among which nitrogen metabolism and photosynthesis are over-represented as functional groups, suggesting CLI186 is a master regulator of metabolism genes. Our analysis also uncovers new insights on the functioning mechanism of the histone methyltransferase CLI186.

Studies of Photosynthetic Reaction Centers and Biomimetic Systems

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Funding:	$195,000

PROGRAM SCOPE

The photosynthetic protein PSII drives the reduction of quinone with electrons obtained from the oxidation of water at the unique Oxygen Evolving Complex (OEC). This process separates charge more than 30 Å across the protein and adds one proton/photon to the transmembrane proton gradient. The overall goals of the project are to apply multiple simulation tools to the analysis of PSII and Rubisco to understand how the protein controls reaction thermodynamics and kinetics. The OEC is to be analyzed to determine the structure of the Mn_4O_5Ca cluster in the 4 S states; the sequence of proton loss from the bridging and terminal oxygens in the cluster and in the surrounding protein; and the pathway for proton release from the OEC. Studies of the quinone acceptor side of PSII analyze the control of electron and proton transfer to the secondary quinone. The free energy and pathways of alternative electron and proton transfers are being investigated.

FY 2012 HIGHLIGHTS

Water Oxidation in PSII: A combined Monte-Carlo/Quantum Mechanics Molecular Mechanics (MC-QMMM) approach together with Extended Absorption Fine Structure simulation is providing a new structure for the S0 state within the OEC and the structure changes moving through the S state cycle. One Mn atom gets oxidized and an Oxygen atom becomes deprotonated during the shortest time step of the entire cycle in good agreement with previous kinetic and electrostatic measurements that concluded the S0 to S1 transition is indeed a proton coupled electron transfer and therefore sensitive to pH and H-isotopic exchange. Parallel studies developed methods to use NAMD MD to bring the OEC structure into agreement with EXAFs measurements. A new, empirical method that analyzes Mn complexes using parameters derived from model systems is being used to analyze the OEC in the S1, S2 and S3 states given the DFT optimized cluster geometry. The likely order of oxidation of the 4 Mn in the OEC as well as the order of oxidation of the bridging and terminal oxygens is determined by Monte Carlo techniques. The perturbation of the complex by the protein can be clearly seen. Analysis of a group of mutants is being used to probe the role of Cl to modulate OEC function.

Quinone Reduction in PSII: Computational models indicate that the first electron transfer only occurs after the protonation of the Ser264-His252 dyad linking one side of the QB site to a protrusion of water molecules from the stroma. Based on electronic structure and molecular dynamics calculations, we show that a dynamic hydrogen bond network is essential to shift the His252 pKa to favor the protonated state upon PQ binding.

Amidase Mediated Modulation of N-Acylethanolamine (NAE) Signaling

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PROGRAM SCOPE

Research in our labs, supported since 2005 by Basic Energy Sciences, has led to the discovery of a new lipid mediator pathway that influences phytohormone 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 plethora of physiological and behavioral processes in mammals, suggesting that the metabolism of NAEs is an important regulatory feature of eukaryotic biology. The current evidence in plants points to interaction between NAE metabolism and ABA signaling, and here we focus our efforts mainly on the transition from embryonic development to seedling establishment and the acquisition of photoautotrophic growth. Our results suggest that NAE metabolism influences chloroplast development and root elongation during seedling establishment and may operate as part of a process to synchronize early plant growth and the assembly of photosynthetic systems. The long term impact of this work will shed light on the fundamental biochemical and molecular mechanisms that control the assembly of photosynthetic machinery in plant systems.

FY 2012 HIGHLIGHTS

During the year, 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. In the coming period, we are attempting to identify by transcriptional profiling the molecular machinery that is responsible for these seedling changes, particularly with respect to the assembly and disassembly of chloroplasts.

Molecular Regulation of Photosynthetic Carbon Dioxide Fixation in Nonsulfur Purple Bacteria

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PROGRAM SCOPE

The goal of this project will be to probe the molecular regulation of CO_2 fixation in nonsulfur purple (NSP) photosynthetic bacteria. Two systems are studied. In *Rhodobacter sphaeroides*, CbbR and RegA (PrrA) are transcriptional regulators of the cbb_I and cbb_{II} (Calvin-Benson-Bassham) CO_2 fixation pathway operons. Both proteins interact specifically with promoter sequences of the *cbb* operons. 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. We recently demonstrated that CbbR and RegA interact and form a discrete complex *in vitro*, as illustrated by gel mobility shift experiments, direct isolation of the proteins from DNA complexes, and chemical cross-linking analyses. For CbbR/RegA interactions to occur, CbbR must be bound to the DNA, with the ability of CbbR to bind the cbb_I promoter enhanced by RegA. Conversely, RegA interactions with CbbR did not require RegA to bind the cbb_I promoter. Currently, we are engaged with detailed studies to define the amino acid residues important for specific interactions with target DNA sequences as well as to define how the two transcriptional regulator proteins, CbbR and RegA, interact with each other.

A somewhat different situation occurs in *Rhodopseudomonas palustris* CGA010, as CbbR interacts with two unusual response regulators (from a different two-component system) that cannot by themselves bind to DNA. Here, CbbR specifically controls transcription of the *cbbLS* genes encoding form I RubisCO. Previous genetic and physiological studies had indicated that this unique two-component (CbbRRS) system influences CbbR-mediated *cbbLS* transcription under conditions where CO_2 is the sole carbon source. We have recently established direct protein-protein interactions between the response regulators of the CbbRRS system and CbbR, using a variety of techniques, and we have documented the ability of specific metabolites to influence response regulator binding to target DNA.

We have also shown that regulation o*f cbb* gene expression is influenced by the nitrogen fixation (*nif*) system via a putative competition for specific metabolites in *Rb. sphaeroides*. We have also probed the potential of another protein (CbbX) to influence *cbb* gene transcription. The long-term impact of these studies will be to completely understand CO_2 fixation control in these model systems for future applications.

FY 2012 HIGHLIGHTS

We have defined and examined how specific transcription regulator proteins interact with target DNA sequences to control transcription of (*cbb*) genes required for CO_2 fixation. There appear to be two types of response regulators, depending on the system; but in all cases, the master regulator protein is CbbR. Specific amino acid residues of CbbR were found to modulate transcription activity in either a positive or negative manner, enabling a fine-tuning of c*bb* gene transcription.

Regulation of the Inorganic Carbon Concentrating Mechanism (CCM) in Cyanobacteria

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Funding:	$162,783

PROGRAM SCOPE

Inorganic carbon is the major macronutrient required by organisms utilizing oxygenic photosynthesis for autotrophic growth. Aquatic photoautotrophic organisms are dependent upon a CO_2 concentrating mechanism (CCM) to overcome the poor CO_2-affinity of the major carbon-fixing enzyme, ribulose-bisphosphate carboxylase/oxygenase (Rubisco). The CCM involves the active transport of inorganic forms of carbon (C_i) into the cell to increase the CO_2 concentration around the active site of Rubisco. Here, the inducible CCM is studied to understand how it is integrated with the light and dark reactions of photosynthesis. The basic hypothesis was that a tight integration is achieved through specific regulatory interactions between photosynthetic metabolites and the transcriptional regulatory proteins that control the expression of the structural genes for the inducible CCM. While such interactions had been hypothesized, the actual mechanisms had remained unresolved. The analysis revealed that metabolic intermediates of the light and dark reactions, notably $NADP^+$ and α-ketoglutarate (α-KG), of cyanobacterial photosynthetic metabolism act as allosteric effectors of the DNA-binding proteins which modulate the expression of the CCM genes. We have been conducting experiments to test the hypothesis that the depletion of *$NADP^+$ and α-KG* results in the de-repression CCM transcriptional expression to alleviate the scarcity of inorganic carbon (Ci).

FY 2012 HIGHLIGHTS

The $NADPH/NADP^+$ ratio now appears key in the coordination of the expression of the CCM, carbon status, and the light reactions which we published this year [Daley et al, Regulation of the Cyanobacterial CO_2-Concentrating Mechanism Involves Internal Sensing of $NADP^+$ and α-Ketogutarate Levels by Transcription Factor CcmR. 2012 PLoS ONE 7(7): e41286]. Using spectroscopic techniques, we have gone on to begin to test the allied hypotheses that carbon limitation affects the redox state of the PQ and the NAD(P)H pools reflecting the progressive filling of metabolite capacity with electrons generated by the light reactions in the absence of an effective sink. This leads to a congestion of the normal routes of photosynthetic electrons that occur as inorganic carbon, the destination of photosynthetic reduction, becomes limiting. We think of this as diminished *absorptive flux capacity.* These spectroscopic signal transients are rich in information, and we are attempting to understand these features. Of particular interest is the post-actinic overshoot of the steady-state $NADPH/NADP^+$ ratio in C_i replete cells. The emerging goals of the project include better understanding of the spectroscopic transients to track and manipulate photosynthetic metabolism. Having real-time data of key metabolites will become important as researchers validate metabolic models and attempt to re-route metabolism for the production of desired products.

Light Energy Transduction in Green Bacteria

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PROGRAM SCOPE

This project focuses on “green bacteria,” diverse organisms from the phyla *Chlorobi*, *Chloroflexi*, and *Acidobacteria*, which synthesize bacteriochlorophyll (BChl) *c*, *d*, or *e* and use these BChls to assemble chlorosomes, remarkably efficient light-harvesting organelles. The long-term objectives of this research program are to understand the design principles of chlorosomes, i.e., their structure, function, and biogenesis. Chlorosomes are an important model system because the self-assembly properties of the BChls occurring in chlorosomes can be exploited in designing biomimetic systems. To maximize the utility of such systems, it is critically important to understand the underlying structural and functional bases for the complexity of chlorosome components, which include extensive modifications of BChl side chains and esterifying alcohols; carotenoid diversity and functions; the presence and function of quinones, glycolipids, and wax esters; and the proteins of the chlorosome envelope. To investigate the ecophysiological and metabolic capabilities of green bacteria, we employ genome sequencing, comparative bioinformatics and genomics, genetics, biochemistry, biophysics, and structural biology approaches. Ongoing work focuses on BChl *e* biosynthesis, carotenoid biosynthesis, and structural and functional studies on the reaction centers of aerobic thermophilic green bacteria.

FY 2012 HIGHLIGHTS

We have developed a conjugation-based, genetic system for *Chlorobaculum limnaeum*, which synthesizes BChl *e* and the aromatic carotenoid, isorenieratene. To facilitate using this model organism, we completely sequenced its genome. We have inactivated *crtU*, *cruA*, *bchU*, and a gene encoding a radical-SAM-like protein thought to play a role in the synthesis of BChl *e*. The *bchU* mutant produces BChl *f*, the first time this pigment has been produced biologically. Chlorosomes containing BChl *f* resemble those containing BChl *e*, but energy transfer to the baseplate BChl *a* molecules is very inefficient, probably explaining why this BChl does not occur naturally. Structural studies on chlorosomes using solid-state NMR methods have been initiated with our collaborators in Leiden. The mutant lacking the radical-SAM protein produces BChl *c*. This establishes that this protein is required for BChl *e* biosynthesis and that it participates in the first committed step in the oxidation of the C-7 methyl group of BChl *c* to the C-7 formyl group found in BChl *e*. We have also overproduced BciB, 8-vinyl protochlorophyllide *a* reductase, from *Chloroherpeton thalassium* in *Escherichia coli*. The recombinant enzyme can reduce the 8-vinyl group of 8-vinyl protochlorophyllide *a* to produce protochlorophyllide *a*. BciB uses electrons provided by reduced ferredoxin, and contains at least one, but more likely two, Fe/S clusters in addition to an FAD cofactor. Efforts to obtain an axenic culture of *Candidatus Chloracidobacterium thermophilum* are still in progress. We are now able to cultivate this organism on solid media, have eliminated the contaminating *Meiothermus* spp., and are currently attempting to eliminate the last contaminant, *Anoxybacillus* spp.

The Type I Homodimeric Reaction Center in *Heliobacterium Modesticaldium*

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PROGRAM SCOPE

This project involves study of the protein and cofactor composition of the homodimeric Type I RC found in heliobacteria and green sulfur bacteria. We have focused primarily, although not exclusively, on the former because it is the simplest Type I RC and because so little is known. The species *H. modesticaldum* was chosen because it is a thermophile and its genome has been sequenced. We used biochemical fractionation and reconstitution protocols along with NMR and time-resolved optical spectroscopy to uncover the properties of Heliobacterial reaction center.

FY 2012 HIGHLIGHTS

The preparation of HbRC cores we previously published was sufficiently pure for spectroscopic studies; but it contained a few protein contaminants and was, therefore, too impure for crystal growth. In the current grant period, we improved on the purification by adding a cation exchange chromatography step. We found that this removed the contaminating proteins, which were identified by mass spectrometry to be membrane-bound cytochrome c_{553} and four different ABC-type transporters. The purified $PshA_2$ homodimer was found to bind 20 BChl *g*, two BChl *g'*, two 8^1-OH-Chl a_F, and one 4,4'-diaponeurosporene. The ratio of 22 (BChl *g/g')*/P_{800} agrees well with the 21.6 ± 1.1 (BChl *g/g'*) /P_{800} determined earlier by a method that used as its basis the 4 irons and 4 sulfurs associated with F_X in each HbRC core. There are ~1.6 menaquinones per HbRC in the high-purity preparation. The HbRC core was active in charge separation and exhibited a trapping time of 23 ps as judged by time-resolved fluorescence studies. The decay of the charge separated states was ~15 ms, as seen earlier. We also discovered that high-purity HbRCs were very stable and could be purified without conversion of BChl *g* to Chl *a* in the presence of O_2 under very low light intensities. In collaboration with Dr. Jörg Matysik (U. of Leiden), we carried out photochemically induced dynamic nuclear polarization (photo-CIDNP) studies of whole cells of *Heliobacterium mobilis*. The purpose of the study was to determine whether the conversion of BChl *g* to Chl a_F affects the ability of the HbRC to carry out primary charge separation. Our studies showed that the chemical shifts of the absorptive and emissive signals remain almost identical between the native samples and those in which ~90% of the BChl *g* had been converted to Chl a_F. These observations are best explained if the primary electron donor (P_{800}) remains unchanged, while the intermediate accessory pigment is converted from BChl g to Chl a_F. Thus, it appears that primary charge separation is retained after conversion of the majority of BChl g to Chl a_F.

Membrane-Attached Electron Carriers in Photosynthesis and Respiration

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PROGRAM SCOPE

The long-term goals of our work are to define the nature, mechanism of function, and biogenesis of cytochromes (cyts) on a molecular level. Cyts are ubiquitous hemoproteins that are key elements in Photosynthesis (Ps) and Respiration (Res) and signal transduction (apoptosis) pathways. Our aim is to elucidate the mechanisms of biogenesis of cyts *c* and their assembly into mature electron transfer (ET) complexes, using phototrophic bacteria (*Rhodobacter*) as an experimental model. The study of Cyt *c* maturation (Ccm), which is the covalent attachment of the heme cofactor to an apocyt *c* to produce mature (holo)cyts, is very important for our understanding of the energy transduction pathways.

Ccm is a widespread process found virtually in all organisms. Ccm-System I is composed of up to 10 membrane-bound proteins (CcmABCDEFGHI and CcdA) and occurs in bacteria, archaea, mitochondria of plants, and red algae. Our recent work uncovered that *R. capsulatus* CcmI, works as an apocyt *c* chaperone during heme ligation, binding to the C-terminus of the apocyt *c* substrates. Ongoing work is focused on the physical interactions of the apocyt *c* with the CcmFHI complex and the heme chaperone CcmE. We found that CcmE recognizes the apocyt *c* even in the absence of heme and forms a ternary complex with CcmI and apocyt *c*. Our data indicate that CcmFHI, CcmE and apocyt *c* form a multisubunit complex during Ccm. We also studied substrate recognition by Ccm-System III, found in mitochondria of fungi, metazoans, and some protozoa. This system includes only one or two Cyt *c* Heme Lyases (CCHL) with different substrates specificities. *Saccharomyces cerevisiae* CCHL only ligates heme to apocyts *c* of eukaryotic origin. Our work revealed that there is a consensus aminoacid sequence within the apocyt *c* N-terminus that is required for CCHL recognition. Thus, we engineered a prokaryotic apocyt *c* as an efficient CCHL substrate just by mutation of two aminoacid residues at its N-terminus.

In the future, we will investigate if the CcmABCD proteins are also involved in heme ligation together with CcmFHI, CcmE and apocyt *c*, as a large multisubunit Ccm complex. Furthermore, we also will explore how the Ccm components recognize and interact with other apocyt *c* substrates, such as the membrane-anchored apocyt c_1 or soluble apocyt *c*'.

FY 2012 HIGHLIGHTS

We have found that CcmE recognizes apocyt *c* in the absence of heme and forms a multisubunit complex with the heme ligation components CcmFHI and apocyt *c* in *R. capsulatus*. Furthermore, we extended our studies to the *S. cerevisiae* CCHL (Ccm-System III) and showed that this enzyme recognizes a specific amino acid sequence located at the N-terminus of the apocyts *c* substrates.

Novel Photoprotection Mechanisms in Closely Packed Photosynthetic Antenna Complexes and in Artificial Light-Harvesting (Bacterio)Chlorophyll Aggregates

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Funding:	$133,739

PROGRAM SCOPE

The main goal of the project is the investigation of a novel photoprotection mechanism employed by some natural photosynthetic proteins that does not require the presence of carotenoids and involves triplet exciton formation in systems of closely packed chlorophyll or chlorophyll-like molecules. The energy of triplet excitonic states is significantly lowered due to excitonic interactions, which prevents triplet energy transfer to molecular oxygen and the formation of highly reactive singlet oxygen. The project also aims at developing the general basis for realizing this novel photoprotection mechanism in artificial light-harvesting devices.

FY 2012 HIGHLIGHTS

For the first time, the triplet state energies of ten major forms of (bacterio)chlorophylls found in nature were directly characterized by the use of a newly built, highly-sensitive, time-gated phosphorescence spectrometer (triplet state energies for only few (B)Chls were measured before). This serves as a basis for triplet exciton energy calculations and evaluation of its photoprotection role in natural and artificial systems. The experiments on natural Fenna-Matthew-Olson (FMO) pigment-protein complexes, which do not contain carotenoids, have also revealed that triplet energy transfer from Chls to oxygen is blocked, suggesting that the triplet exciton formation is a sole photoprotection mechanism in these complexes. The triplet exciton simulations of FMO are under way. The classical diffusion simulations of oxygen content in functioning photosynthetic cells are complete. Manuscripts on these findings are in preparation for publication.

Regulation of Actin Filament Ends: The Role of Capping Protein in Stochastic Dynamics

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Funding:	$170,000

PROGRAM SCOPE

A network of highways and byways in plant cells is constructed from actin filaments. These serve as dynamic tracks for the transport and delivery of diverse cargoes, including non-cellulosic wall polysaccharides to the cell wall. Our overall goal is to understand the molecular mechanisms that underpin actin filament construction and turnover. Specifically, we will investigate the properties and function of the heterodimeric actin capping protein from *Arabidopsis* (CP). To understand how actin filaments are organized and turn over *in vivo*, we applied variable-angle epifluorescence microscopy (VAEM) to living epidermal cells expressing an actin reporter. In the first quantitative description of single actin filament dynamics in plant cells, we found that filaments grow extremely rapidly but are rather short-lived. Filament disassembly is mediated by prolific severing activity rather than depolymerization from ends. A new model, based on the biochemical/biophysical properties of plant actin and actin-binding proteins, was developed to describe this stochastic dynamic behavior. In this project, we aim to test the hypothesis that loss of CP leads to increased actin polymer levels and changes the availability of filament ends in living cells, thereby altering actin array architecture and filament dynamics.

FY 2012 HIGHLIGHTS

Using reverse-genetics in *Arabidopsis* and state-of-the-art imaging approaches, we examined the phenotype of three homozygous *cp* knockdown mutants. Consistent with our hypothesis, reduced CP leads to increased availability of filament ends in living cells. Specifically, we observed an up to six-fold increase in filament–filament annealing as well as a significant increase in the origin of new filaments from filament ends. Overall, this results in a marked enhancement of actin filament density in the cortical array of epidermal cells, which can be inferred to be due to enhanced actin polymerization. To test whether CP is negatively regulated by the structural and signaling lipid, phosphatidic acid (PA), we elevated PA levels artificially in wild-type plant cells and observed the effect on actin organization and dynamics. Increased PA levels phenocopy the *cp* knockdown phenotype, consistent with phospholipids inhibiting the function of CP *in vivo*. Moreover, if CP is a major biosensor of PA in cells, translating lipid signals into changes in cytoskeletal architecture, then *cp* mutants should be blind to changes in PA levels. This is indeed the case; *cp* mutants do not respond to either exogenous PA additions or reduction in PA through inhibition of phospholipase D activity. These findings provide the first evidence that CP is a PA biosensor in eukaryotic cells and that regulation of filament ends is a key facet of the stochastic dynamic turnover of cytoskeletal tracks.

Elucidating the Principles that Control Proton-Coupled Electron Transfer Reactions in the Photosynthetic Protein, Photosystem II: A Model for Design of Bio-Inspired Photocatalytic Water-Splitting

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Funding:	$160,000

PROGRAM SCOPE

The objectives of our research program are to understand the tuning and regulation of PCET reactions of PSII and to elucidate their role in the early charge-transfer steps of photosynthesis. We are determining the factors that control the coupling of proton (PT) and electron transfer (ET) pathways in PSII by developing new state-of-the-art, multi-dimensional and time-resolved nuclear magnetic resonance (NMR) and electron paramagnetic resonance (EPR) spectroscopy methods. This research addresses the urgent need for bio-inspired molecular assemblies for new and efficient catalysts for solar fuels production that incorporate multi-electron transfer and PCET reactions.

FY 2012 HIGHLIGHTS

(1) The binding and activation of substrate water molecules in the oxygen-evolving complex of photosystem II. (a) Experiments provide, for the first time, a direct handle with which to monitor the activation and catalysis of the substrate water molecules in the solar water oxidation reaction. [Energy Environ. Sci., 5, 7747 2012)]. (b) By exploiting the power of 2D ^{1}H HYSCORE spectroscopy, for the first time, we detect the protons that are weakly hyperfine coupled to the Mn_4Ca-oxo cluster in the S_2 state of Sr^{2+}-substituted PSII. [Manuscript Submitted (2012)]. (c) We have quantitatively characterized the weak magnetic interactions between protons of two terminal water ligands and the paramagnetic dimanganese ‘di-μ-oxo’ core of 1 using 2D ^{1}H and ^{14}N HYSCORE spectroscopy [*J. Phys. Chem. B*, 115, 12220 (2012); *Phys. Chem. Chem. Phys.*, 14, 7090 2012].

(2) The tuning and control of quinone cofactors in photosynthetic protein complexes. (a) We have conducted a systematic study of the principal components of the g-tensors of a library of model benzosemiquinone anion radicals in both protic and aprotic solvents using high-frequency 130 GHz EPR spectroscopy [*J. Phys. Chem. B*, 116,676 (2011)]. (b) We have utilized high-resolution 2D ^{1}H and ^{14}N HYSCORE spectroscopy to directly probe the strength and orientation of the hydrogen bonds of the Q_A^- state with the surrounding protein environment of PSII [*Biochemistry*, 50, 491 (2011)]. (c) The ^{1}H HYSCORE experiments indicate that A_{1A}^- forms a single out-of-plane hydrogen bond; the ^{14}N HYSCORE spectroscopy experiments support a backbone amide nitrogen as the hydrogen bond donor [*Biochemistry*, 50, 3495 (2011)].

(C) The functional specificity of the tyrosine residues of PSII: Mechanism of proton-coupled electron transfer at Y_Z and Y_D. To elucidate the mechanism of PCET at the Y_D residue, we have developed pulsed HF ENDOR spectroscopy methods to structurally characterize the $Y_D^{\bullet}$ PCET intermediates of PSII that afford valuable information on the mechanism of PCET [Manuscript Submitted (2012)].

Analysis of Ethylene-Regulated Growth Networks in Arabidopsis

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Funding:	$200,000

PROGRAM SCOPE

Although many significant insights have been gained into the mechanisms of plant growth and biomass production, major unanswered questions still remain about how plants integrate the various environmental and endogenous signals to control their growth. The goal of this project is to identify new hormone signaling pathway components and the major transcriptional gene targets for plant growth regulators with a focus on ethylene gas. In particular, we will use a variety of types of experimental approaches, including genomics, genetics, and biochemistry, to explore the hormone signaling pathway targets, their roles in ethylene signaling, and cross-regulation with other hormone response pathways. Our hypothesis is that, through the identification and analysis of hormone pathway transcriptional targets, we will be able to functionally dissect the various transcriptional output pathways of ethylene that control the numerous and important biological processes regulated by this simple gas, including increasing biomass production, biotic and abiotic stress, senescence, and many other processes controlled by this hormone.

The highly conserved master regulatory transcription factor called ETHYLENE INSENSITIVE3 (EIN3) is both necessary and sufficient for activation of all plant ethylene responses, and its cross-regulation with other hormone signaling pathways and light have profound effects on the regulation of plant growth and development. The research objectives are to understand the role of EIN3 in the ethylene signaling network and how its targets function to communicate with other hormone signaling networks and light. Specifically, we plan to identify and characterize EIN3-dependent ethylene response output pathways, and identify and determine the roles of additional ethylene signaling components in the regulation of EIN3. The long-term goal of this project will be to develop plants with improved bioenergy characteristics such as increased biomass, improved stress tolerance, and better resistance to pests and pathogens.

FY 2012 HIGHLIGHTS

We have successfully identified thousands of new EIN3 gene targets and made great strides toward understanding of the ethylene regulatory network in seedling. Specifically, we characterized the dynamic ethylene transcriptional response by identifying targets of the master regulator of the ethylene signaling pathway (EIN3) using chromatin immunoprecipitation sequencing and transcript sequencing during a time-course of ethylene treatment. Ethylene-induced transcription occurs in temporal waves regulated by EIN3, suggesting distinct layers of transcriptional control. EIN3 binding was found to modulate downstream transcriptional cascades, feedback circuitry of the ethylene signaling pathway, and interconnections between hormone response pathways, linking the regulation of growth and development by ethylene to many new biological processes in previously unknown ways.

Signal Transduction Pathways that Regulate *CAB* Gene Expression

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PROGRAM SCOPE

Chloroplasts are the sites of synthesis of diverse chemicals, as well as sensors of environmental stress. The goal of our project is to define the signaling pathways from chloroplasts that regulate nuclear gene transcription. We have identified signals or signaling components from three different retrograde signaling pathways: one that arises from the tetrapyrrole pathway, one from a plastid gene expression pathway, and a third signal generated by a change in redox of the plastoquinone pool (e.g., stress from excess light). A genetic screen for *retrograde signaling* mutants identified six genes, which acted at the branch point between Chlorophyll and heme biosynthesis in the porphyrin biosynthetic pathway. Our data may be explained by one of two models. In the first model, accumulation of Mg-ProtoIX generates a signal from damaged plastids, which then represses the expression of hundreds of photosynthetic genes through the regulator, ABI4. We also have data for a second model in which heme accumulates in the cytosol, generating a positive signal from healthy plastids to maintain nuclear gene expression. Completion of the proposed projects should provide an increased understanding of the retrograde signaling pathways that control expression of hundreds of nuclear genes in response to the functional state of chloroplasts. These studies will influence our abilities to manipulate plant growth and development, and will aid in the understanding of the developmental control of photosynthesis, a central biological process that is the source of energy for all photosynthetic organisms and, via the food chain, for all other forms of life. Knowledge of the control of chloroplast development is crucial to our quest for an abundant food supply and cheap sources of energy.

FY 2012 HIGHLIGHTS

We have published a paper establishing heme as a positive signal from healthy chloroplasts, as well as a second paper in which we utilized mutations in plastid polymerase to generate a plastid signal without the use of herbicides. The second study validates our use of herbicides in the original genetic screens. We have performed a second genetic screen on a weak allele of *fc1* and have isolated 10 new genetic loci that may be involved in heme signaling. We are in the process of identifying the causal mutations in these strains using cloning by sequencing methodologies. In addition, we have identified mutations in seven new genes involved in high light stress.

Eukaryotic Initiation Factor 3 (EIF3) and 5' mRNA Leader Sequences as Agents of Translational Regulation in Arabidopsis

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

PROGRAM SCOPE

Protein synthesis, or translation, consumes a sizable fraction of the cell's energy budget, estimated at 5% and up to 50% in differentiated and growing cells, respectively. Plants also invest significant energy and biomass to construct and maintain the translation apparatus. Translation is regulated by a variety of external stimuli. Compared to transcriptional control, attributes of translational control include reduced sensitivity to stochastic fluctuation, a finer gauge of control, and more rapid responsiveness to environmental stimuli. Yet, our murky understanding of translational control allows few generalizations. Consequently, translational regulation is underutilized in the context of transgene regulation. We also know little about the contribution of translational control to plant diversification, including the suitability of different plants as bioenergy sources.

This project seeks to unravel how an emerging regulatory mRNA sequence element, upstream open reading frames (uORFs), is integrated with the general translation initiation machinery to control translational efficiency and to permit translational regulation on specific mRNAs. Previous DOE-supported investigations have highlighted that translational control by uORFs is mediated in part by eIF3h, one of 12 subunits of the largest and arguably least understood of the eukaryotic initiation factors.

This project will dissect the contributions of uORFs and eIF3 to translational efficiency in plants. (1) Two complementary computational models of the translation initiation process will be developed to rigorously test hypotheses concerning the individual molecular functions of eIF3h. (2) Molecular activities will be assigned to eIF3 subunits other than eIF3h by combining translation assays in Arabidopsis *eif3* mutants with numerical models. (3) A novel, transcriptome-wide landscape of translational efficiency will be drawn by deep-sequencing of ribosome-protected mRNA fragments and the data utilized to further characterize the role of uORFs and eIF3 in translation initiation. (4) Finally, we will build a framework for the comparative genomics of uORFs in dicotyledonous plants as a first step toward understanding how the rapid evolution of mRNA sequence elements has accompanied the diversification of plants. In summary, we hope to learn how to harness translational regulation for the directed adaptation of plant genomes in support of new applications in the bioenergy sector.

Optimizing Rubisco Regulation for Increased Photosynthetic Performance under Climate Change

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Funding:	$130,000

PROGRAM SCOPE

Photosynthesis is acutely sensitive to inhibition by moderate heat stress because of the thermal sensitivity of Rubisco's catalytic chaperone, Rubisco activase. The broad goal of this project is to improve the performance of photosynthesis, particularly under moderate heat stress, by (1) introducing more heat stable activases into Camelina sativa, a potential bioenergy crop used in this project as a model system; and (2) identifying the mechanism for regulation of Rubisco activase in species like tobacco that express only the non-redox-regulated form of the enzyme. For the first objective, baseline information was obtained on the temperature optimum of photosynthesis, Rubisco activation, and Rubisco activase activity in camelina. All of these parameters were inhibited at 30°C, indicating that camelina photosynthesis should show improvement from the introduction of the more stable Rubisco activases from cotton and rice. Identifying the mechanism for regulating Rubisco activase, by examining the sensitivity of Rubisco activase from various plant species to inhibition by ADP, will help elucidate the specific role of the two Rubisco activase isoforms. Since cotton, rice, and camelina express both isoforms of Rubisco activase, information on the regulatory properties of each isoform will be used to select the most appropriate Rubisco activase for improving thermal stability. In addition, understanding the regulation of Rubisco activase will provide insights into how to increase the response time of photosynthesis during transitions from low to high irradiance by accelerating the rate of Rubisco activation.

FY 2012 HIGHLIGHTS

Camelina plants have been successfully transformed with both isoforms of cotton and rice Rubisco activase. We have obtained several lines for each construct, under both constitutive and heat-inducible promoters. Five of the lines with cotton Rubisco activase have been advanced to the T3 generation, and this generation is currently being grown for analysis of the thermotolerance of photosynthesis. Experiments comparing the effect of ADP on Rubisco activase activity showed that the non-redox regulated form of Rubisco activase in tobacco was sensitive to inhibition by ADP, and thus differed from this form in Arabidopsis and camelina. The sensitivity of the tobacco enzyme to ADP was reduced markedly by changing 17 amino acid residues to the corresponding residues in Arabidopsis.

Photosynthetic induction upon transition from low to high light in transgenic Arabidopsis plants containing only a non-regulated Rubisco activase was faster than in tobacco and other plants with regulated Rubisco activases. Thus, regulation of Rubisco activase affects the rate of photosynthetic induction. We are currently investigating if this effect can be used to design plants that respond more rapidly to changes in irradiance level.

Disruption of the CO_2 Concentrating Mechanism in C_4 plants: Implications for CO_2 Fixation and Photosynthetic Efficiency during C_4 Photosynthesis

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Funding:	$170,000

PROGRAM SCOPE

The specialized biochemistry and leaf anatomy of C_4 plants results in a high CO_2 concentration within the leaf, significantly increasing photosynthetic energy use efficiency compared with most C_3 plants. While, the efficiency of the CO_2 concentrating mechanism in C_4 plants can be negatively affected by environmental conditions, it is not understood how C_4 photosynthesis responds (both biochemically and structurally) to optimize photosynthetic efficiency. Understanding how the coordination of the C_3 and C_4 cycles, and the diffusion of CO_2 from the bundle sheath cells influences the efficiency of the CO_2 concentrating mechanism in C_4 plants, is critical for accurately modeling the yields of C_4 crops under future climatic conditions. Additionally, this information is important for optimizing the biochemical and structural features of C_4 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 CO_2 fixation in C_4 crop and biofuel species.

The long-term goals of our research are to determine the mechanisms controlling the photosynthetic efficiency of the CO_2 concentrating mechanism in C_4 plants and to be able to capture, store, and mobilize solar energy. The overall objective of this proposal is to determine how changes in the capacity of the C_3 and C_4 cycles and bundle sheath cell wall properties determine the photosynthetic efficiency of the CO_2 concentrating mechanism in C_4 plants in response to changes in light and temperatures. Our central hypothesis is that the efficiency of the CO_2 concentrating mechanism in C_4 plants is optimized through balancing the activity of the C_3 and C_4 cycles with the structural properties of the bundle sheath cells. This hypothesis stems from our preliminary data and previous publications showing that changes in the light and temperature influences the capacity of the C_3 and C_4 cycles to maintain photosynthetic efficiency. We will meet our overall objective by testing our central hypothesis with the following specific aims: (1) determine the mechanisms that disrupt the metabolic coordination of C_4 photosynthesis in response to changes in leaf temperature and (2) determine how changes in the capacity of the C_3 and C_4 cycle control the photosynthetic efficiency of C_4 photosynthesis in response to changes in leaf temperature and light availability.

Enhancement of Photoassimilate Utilization by Manipulation of the Starch Regulatory Enzymes ADPglucose Pyrophosphorylase and Starch Phosphorylase

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Funding:	$180,000

PROGRAM SCOPE

The events that control starch synthesis remain poorly understood. This grant supports research to understand how two enzymes, starch phosphorylase I and ADPglucose pyrophosphorylase (AGPase), control the biosynthesis of the starch precursor and pre-starch granule, respectively. Conversion of the pre-starch granule to the mature form is dependent on AGPase, which produces ADPglucose, the substrate used for starch synthesis. Although considerable information is available on the *in vitro* catalytic and regulatory properties of this enzyme activity from a wide variety of plant sources, much less is known about the structure-function relationships of this enzyme at the molecular level and the role and importance of this enzyme in governing plant productivity. Likewise, the role of the starch phosphorylase Pho1 in starch metabolism is poorly understood. Although Pho1 catalyzes a reversible reaction enabling it to extend or degrade starch, genetic and biochemical studies supported by past DOE grant support provide direct support for a biosynthetic role for this enzyme especially during the initial phase of starch precursor formation. The mechanism by which Pho1 contributes to the initial events of starch biosynthesis is largely unexplored, and efforts supported by this grant are focused at filling this knowledge gap.

FY 2012 HIGHLIGHTS

Past studies have demonstrated that the small subunit (SS) of the heterotetrameric AGPase plays a dominant role in allosteric regulation and catalysis, although optimal enzyme function requires the large subunit (LS) whose role remains elusive. Current efforts are directed at elucidating the 3-D structure of AGPase and how the LS interacts with the activator 3-PGA and substrate ATP via the analysis of wildtype and mutant enzyme forms. In addition to allosteric regulation, ongoing studies have demonstrated that the cereal endosperm enzyme is controlled by redox via modification of the LS. Efforts are now being directed at identifying the regulatory mechanism and its involvement in governing starch biosynthesis during seed development. Past DOE-supported studies showed a direct correlation between leaf starch, photosynthetic capacity, and plant growth in Arabidopsis and rice. To extend these studies, transgenic poplar expressing mutant LS genes are currently being assessed for their growth and biomass properties.

Studies on Pho1 are focused on understanding its regulation and how it participates in starch biosynthesis. Similar to our studies on AGPase, efforts are directed at elucidating its 3-D structure and identifying the AMP inhibitor binding site. Studies have demonstrated that Pho1 interacts stoichiometrically with α-1,4-glucan transferase (D-enzyme) to form a large hetero-octomer complex. An understanding of the kinetic properties of this novel multimeric enzyme complex is likely to provide novel insights on the roles of these enzyme activities in the early events of starch synthesis.

Controlling Electron Transfer Pathways in Photosynthetic Reaction Centers

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Funding:	$194,000

PROGRAM SCOPE

This collaborative SISGR project involves researchers at Washington University in St. Louis (WU) and Argonne National Laboratory (ANL). The Abstract (which starts at the next paragraph) encompasses the overall project. The personnel noted on the form here reflect only the WU team. Note that a technician, who has received considerable training and professional advancement is working on this project at WU (and has now decided to enter graduate school as a result). This point is noted here because there is no category for listing such personnel and is as such listed as a graduate student.

Photosynthetic reaction centers (RCs) convert light energy into chemical energy in a series of extremely efficient electron transfer reactions, accomplishing transmembrane charge separation. The structures of RCs reveal two symmetry-related branches of cofactors that are functionally asymmetric; bacterial RCs use the A pathway exclusively. Using current knowledge of the architectural and energetic factors that underlie the directionality and yields of electron transfer, our hypothesis is that we can generate a mutant RC that uses the B pathway preferentially and efficiently. Site-specific mutagenesis has produced transmembrane charge separation solely via B-branch activity, but the best overall yield of state $P^+Q_B^-$ is still very low (~15%). Insights from previous attempts at rational design have provided neither the means nor understanding necessary to engineer an efficient B-branch electron-transfer pathway. Therefore, the goal of this project is to produce such an RC via directed molecular evolution, implementing streamlined mutagenesis and high-throughput spectroscopic screening steps to sample a large number of RC variants. Our primary experimental vehicle is the RC from the purple photosynthetic bacterium *Rhodobacter (R.) capsulatus*. The effort is being complemented through the mutagenesis of the related RC from the green photosynthetic bacterium *Chloroflexus (C.) aurantiacus*, which bears key differences in cofactors and amino acid sequence.

As noted above, this project involves researchers at Washington University and Argonne National Laboratory. The mutagenesis and protein isolation and purification are conducted in the laboratory of Deborah Hanson and Philip Laible at ANL. The high-throughput time-resolved spectroscopic screening of mutants and ultrafast characterization of the primary events in key resulting mutants are conducted in the laboratory of Christine Kirmaier and Dewey Holten at WU. The Blankenship lab at WU provides DNA for the generation of the *Chloroflexus* mutagenesis system.

FY 2012 HIGHLIGHTS

Advancements have been made in the following areas. (1) On the technical side, we have improved the sensitivity and signal-to-noise ratio of the millisecond-to-seconds high throughput screening assay. The advancements include the ability to perform the assays with samples about one-tenth the concentration as previously. This will greatly facilitate studies going forward. (2) We have screened about 100 new mutants and found a number with enhanced overall yield of B-side charge separation. (3) We have carried out ultrafast transient absorption studies on select mutants and have gained insights into the rates and yields of the specific pathways of charge separation pathways that give rise to the altered overall yields of B-branch electron transfer. Collectively, these findings improve our understanding and ability to engineer an efficient electron transfer pathway (specifically the B-branch) in a photosynthetic reaction center. Such knowledge is applicable to the design of artificial systems for solar energy conversion using inspiration from the native photosynthetic systems.

Redox Factors in the Thylakoid Lumen for Protection and Repair of the Photosynthetic Apparatus

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Funding:	$195,000

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 lumenal 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 and small molecules in photoprotection and repair of the photosynthetic apparatus. During the current funding period, we have determined the critical roles of a number of lumenal redoxin proteins in such mechanisms. We have also unraveled the role of glutathione, a low-molecular weight thiol compound, in redox homeostasis in cyanobacteria. In particular, we have determined the presence of a functional pool of such compounds in the thylakoid lumen. During the next funding period of this project, there are three 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 identify and characterize glutathione transporters in cyanobacterial thylakoid membranes; and (3) to dissect the Redox Proteome of cyanobacterial thylakoid lumen. 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 2012 HIGHLIGHTS

Thus far, we have developed a method for rapid isolation of thylakoid membranes from the cyanobacteria *Synechocystis* 6803 and *Synechococcus* UTEX 2973. We have also generated an initial detailed global map of the redox status of proteins in *Synechocystis* 6803. In the next period, we will refine both of these methods to generate reliable data sets for two publications next year.

The Fmo Antenna Complex From Green Photosynthetic Bacteria

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Funding:	$209,752

PROGRAM SCOPE

All photosynthetic organisms contain a light-harvesting antenna system, which absorbs solar photons and transfers energy to the reaction center complexes where photochemistry takes place; and the energy is stored ultimately in high-energy compounds such as biomass. Photosynthetic antenna complexes are extremely diverse in terms of structural organization and type of pigment utilized, yet all have a similar function of light collection and must operate using the same set of physical principles. The research undertaken in this project centers on the Fenna-Matthews-Olson or FMO antenna protein that is found in anoxygenic green sulfur photosynthetic bacteria. The FMO protein is a model system for photosynthetic antennas and was the first chlorophyll-containing protein to have its x-ray crystal structure determined. It has also been studied in great detail using numerous types of spectroscopic and theoretical methods.

Research includes a variety of structural and spectroscopic studies on the isolated FMO protein derived from several different green sulfur bacteria. In addition, the highly divergent FMO protein from the newly discovered acidobacterium *Candidatus* Chloracidobacterium thermophilum has been analyzed. Additional work centers on using mass spectrometry to elucidate the attachment sites of the FMO protein to both the chlorosome antenna complex that transfers energy to it and the reaction center that receives energy from it. We are working to develop a mutagenesis system for the FMO protein and generate a series of site-directed mutants to better understand how the protein environment determines and influences the electronic properties of the complex. Finally, we plan to examine the pathway and efficiency of the energy transfer step from the FMO protein to the reaction center using selected biochemical preparations and both steady-state and time-resolved spectroscopic techniques. The results of this research project should give us a much improved understanding of the structural and energetic properties of this model antenna complex and also improve our understanding of its location in relation to other parts of the antenna system and how it functions in the energy transfer process.

Amino Acid-Sensing Ion Channels in Plants

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Funding:	$170,000

PROGRAM SCOPE

Plants possess genes homologous to those encoding glutamate-gated ion channels in the central nervous system of animals. In animals, these membrane proteins form hetero-tetrameric channels that conduct cations including K^+, Na^+, and Ca^{2+} into a cell after glutamate binds to them. Elucidating molecular-level activities of the plant glutamate receptors (there are 20 GLRs in Arabidopsis) and testing hypotheses about how they transduce amino acid signals into physiological and developmental responses in the Arabidopsis plant are the topics of this DOE project. It aligns with the goals of the funding program by expanding our understanding of how the amino acid component of photosynthetically-concentrated chemical energy is sensed by the plant.

FY 2012 HIGHLIGHTS

We have demonstrated with the biophysically rigorous technique of patch clamping that the *GLR3.4* gene encodes an ion channel gated (triggered to open) by three amino acids – asparagine, glycine, and serine. We demonstrated that the channel is highly selective for Ca^{2+} over Na^+ and can generate transient Ca^{2+} signals in the cytoplasm. Also at the molecular level, we have shown that GLR3.4 physically interacts with GLR3.2, but not GLR3.3. At the plant level, we have shown GLR3.2 and GLR3.4 are located in the root phloem and, through mutant analysis, that the heteromers they are presumed to form function in the production of lateral root primordia. GLR3.3 is expressed elsewhere in the root and does not participate in lateral root production. GLR3.2 and GLR3.4 are also highly expressed in the developing seed and detected in the vasculature of the funiculus which “feeds” the developing seed. Both GLR3.2 and GLR3.4 participate in seed development, possibly by monitoring the import of amino acids (asparagine is a major free amino acid transported to and accumulated in seeds) because mutating either of the genes increases seed size. One of the new directions the project is taking is biochemical. A portion of the protein hypothesized to bind the gating ligand is being produced for tests of amino acid-binding and ultimately structural studies aimed at understanding the broad amino-acid specificity of the GLRs. Also, studies of the impact of *glr* mutations on free amino acid distributions in the plant are planned.

Molecular Properties and In Planta Functions of the Plasma Membrane Proton Pump (H+-ATPase)

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Funding: $144,535

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 protonmotive force (composed of both a transmembrane electrical potential and a proton chemical gradient) that drives the transport of solutes essential for cell growth. The overall research goal of this project is to use genetic, biochemical, and physiological technologies for understanding the molecular functions 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. Our specific approach is to isolate Arabidopsis mutants and study the phenotype resulting from the genetic defects. We are also using the mutants to perform structure-function studies via rescuing the mutants with site directed mutations via full-length genomic clones containing the regulatory sequences. 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 2012 HIGHLIGHTS

In Arabidopsis and all other plants, this protein is encoded by a family of 11 genes called AHA (**A**rabidopsis **H**-+**A**TPase)'s 1-11. 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. Last year, we published the results of a comprehensive study of the effects of genetically reduced plasma membrane proton pump activity for AHA1 and AHA2 and demonstrated, for the first time, that this is an essential enzyme for vegetative growth. We have recently established a system for obtaining a translationally fused 'tagged' pump that, importantly, rescues growth of the lethal double mutant. We have recently used this tag to purify the active enzyme from plants treated for short periods of time with various effectors (e.g., auxin, fusicoccin). With this tagged enzyme and isotope-assisted methods for quantitation with an LTQ-Orbitrap tandem mass spectrometer, we are identifying and measuring posttranslational changes in the ATPase and other proteins that remain associated with the enzyme after detergent solubilization and purification.

Structure-Function Studies of Photosystem II

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Funding:	$230,000

PROGRAM SCOPE

The objective of this project is to characterize the function of photosystem II (PSII) by using biophysical studies in conjunction with manganese model chemistry. These experimental studies will guide and test computational analyses of PSII carried out in collaboration with Victor Batista (Yale University), Marilyn Gunner (City College, New York) and Doug Bruce/Sergej Vassiliev (Brock University). The recent 1.9 Å x-ray crystal structure of PSII provides a detailed architecture of the O_2-evolving complex (OEC) and the surrounding amino acids. Building on the new structural information, we are carrying out experiments to characterize the function of PSII. Specific goals for this project are to (1)characterize the redox functions of carotenoids and the secondary electron-transfer reactions in PSII and (2) carry out structure-based experiments on PSII to characterize the function of specific residues and the mechanism of the OEC. To achieve our first goal, we aim to (a) study site-directed mutants in which amino-acid residues in PSII predicted to perturb cofactors in the secondary electron-transfer pathways are changed and (b)redirect electron transfer on the acceptor side of PSII in order to utilize the electrons liberated from water oxidation by PSII for photoelectrochemical fuel formation. To achieve our second goal, we aim to (a) investigate the function of chloride in oxygen evolution by studies of anion-substituted PSII and site-directed mutations of D2-Lys317 and (b) use oxygen isotope studies to gain insight into how the substrate waters are bound and activated for reaction in the OEC.

FY 2012 HIGHLIGHTS

We have probed the secondary electron-transfer pathway in PSII by site-directed mutagenesis of the D2 subunit around the binding pocket of Car_{D2} (D2-G47W, D2-G47F, and D2-T50F mutants were generated in *Synechocystis* sp. PCC 6803 by Peter Nixon, Imperial College). PSII from these mutants has been characterized by near-IR and EPR spectroscopy, showing that Car_{D2} is the initial donor in secondary electron transfer and allowing the assignment of the spectral signatures of the Car_{D2} radical cation. Moreover, these mutations cause PSII to have a higher susceptibility to photodamage, linking the secondary electron-transfer pathway to photoprotection. We have also studied the role of chloride in the OEC by investigating site-directed mutations of D2-K317, which forms an ion pair with chloride (D2-K317A, D2-K317Q, and D2-K317E mutants were generated in *Synechocystis* sp. PCC 6803 by Richard Debus, University of California, Riverside). Steady-state oxygen evolution measurements show that D2-K317A-mutated PSII is independent of chloride, as we hypothesized last year based on analogy to other chloride-activated enzymes. PSII from these mutants has been characterized by FTIR and EPR spectroscopy; and the flash-dependent yield of O_2 has been measured, showing that proton transfer is inefficient in D2-K317-mutated PSII.

DOE National Laboratories

Biomimetic Hybrid Architectures for Solar Chemical Energy Conversion

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Funding:	$883,000

PROGRAM SCOPE

The goal of this program is to develop new classes of biomimetic hybrid architectures for solar fuels applications by combining biological and chemical synthetic methods. The program targets the creation of supramolecular ensembles tuned for multi-electron transfer photochemistry that are too complex to be approached with chemical synthesis alone, but are amenable for detailed chemical and biological modification and high-resolution structure-function analyses. The program exploits emerging work on the discovery, expression, and genetic manipulation of remarkable "molecular wire" architectures designed by Nature for multi-electron transfer and catalysis, and develops synthetic supramolecular chemistry methods to augment these frameworks with light-harvesting pigments and active-site transition metal complexes to achieve molecular hybrids with new catalytic functionalities.

Fundamental energy conversion processes are investigated using forefront time-resolved synchrotron x-ray, optical, and electron paramagnetic resonance (EPR) measurements that dynamically resolve electronic and coordinate structures of the active-site, metal-complex guests within biomimetic hosts frameworks on functional time scales. This program will resolve fundamental mechanisms for coupling multiple-electron catalysis to excited-state photochemistry, and provide a path to design new catalysts based on biological host-guest chemistry with sustainable atomic compositions.

FY 2012 HIGHLIGHTS

A comparison was made between electrostatic self-assembly and covalent linking of photosensitizers as strategies for adding light-initiated electron transfer chemistry to multiheme c-cytochromes recruited from the Geobacter genome. Water-soluble anion porphyrins were found to serve as bridging ligands nucleating multimerization of the complimentarily charged protein. The final aggregation products suggest that multimerization involves a combination of electrostatic and hydrophobic interactions. Zinc and free base porphyrins showed efficient excited-state quenching without electron transfer in the cytochrome-porphyrin assemblies. The results demonstrate an overlooked complexity in the design of multifunctional ligands interactions for protein surface recognition. In contrast, covalently linked assemblies using ruthenium tris-bypyridyl derivatives covalently linked to cysteine residues placed at a variety of positions on the Geobacter PpcA cytochrome c_7 showed efficient light-induced electron transfer with position-dependent lifetimes. This work has established foundations for the design of hybrid architectures for solar fuels catalysis.

An Integrated, Super-Resolution Characterization of Natural Photosynthesis: Operating Principles, Structure, Regulation and Repair

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Funding:	$930,000

PROGRAM SCOPE

In plants and algae, the photosynthetic membrane of 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 photosynthetic membrane, the regulation of its composition, and the membrane dynamics occurring during photosynthetic regulation and repair. We use 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 2012 HIGHLIGHTS

Several electron microscopy preparations and techniques were used to describe the different levels of organization of thylakoids in situ within plant leaves, in chloroplasts extracted from plant tissue, or as isolated thylakoid stacks (grana). Tapping-mode atomic force microscopy (TM-AFM) imaging of spinach grana membranes in air provided information about the basic organization of PSII supercomplexes. Imaging of the same type of membranes in buffer allowed us to characterize the lumenal and stromal faces in the thylakoid stack. We have used a different AFM system, which is capable of measuring dynamic mechanical responses (height, elasticity, and viscosity) of samples, to measure thylakoid membrane behavior in response to different illumination conditions. To visualize the PSII repair process in the thylakoid membrane, we have completed the design and construction of a microscope that combines stimulated emission depletion and fluorescence lifetime imaging. In computational modeling work, we showed that the lipid environment has a crucial effect in determining the cross-angle distribution of packed transmembrane helices and is at least as important in shaping the interaction of these helices as specific amino acid residues.

Energy Conversion in Photosynthesis - Mechanism of Water Oxidation and Oxygen Evolution

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Funding:	$1,021,000

PROGRAM SCOPE

Oxygen, which supports all aerobic life, is abundant in the atmosphere because of its constant regeneration by photosynthetic water oxidation by green plants, algae, and cyanobacteria. The light-induced oxidation of water, catalyzed by a Mn_4Ca cluster associated with the Photosystem II complex to dioxygen, is one of the most important chemical processes occurring on such a large scale in the biosphere. In our ongoing investigations of the Mn oxidation-state changes, the electronic and geometric structure, and the role of the cofactors Ca and Cl, we have made extensive use of x-ray and EPR spectroscopy. We are using high-resolution absorption and emission x-ray spectroscopy, including resonant inelastic x-ray scattering spectroscopy, to study single-crystals and solutions of PS II and inorganic models. We will use the new femtosecond X-ray Laser Facility at Stanford, to simultaneously collect x-ray diffraction and x-ray emission spectroscopy of the intermediates states in a time-resolved manner to capture short-lived intermediates and the step that includes the O-O bond formation. The x-ray laser will also be used for time-resolved Mn L-edge spectroscopy studies of the intermediate states to understand the electronic structural changes during the catalytic cycle. These techniques elucidate the changes in the geometric and electronic structure of the catalyst as it cycles through the intermediate states, which will lead to an understanding of the mechanism. The insights gained from photosynthesis can then be applied in the design of artificial solar-energy based devices to split water and will contribute to our search for cleaner, renewable carbon-neutral energy sources.

FY 2012 HIGHLIGHTS

We used the x-ray free electron laser at Stanford to collect, simultaneously, x-ray spectroscopy and x-ray diffraction data from microcrystals of photosystem II at room temperature. The results show that the “probe before destroy” approach of LCLS works even for the highly-sensitive Mn_4CaO_5 cluster in PS II. This work is the first important step toward future studies for resolving the structure of the Mn_4CaO_5 cluster without any damage at room temperature, and of the reaction intermediates of PS II during O-O bond formation.

We also received beamtime at the x-ray laser for Mn L-edge experiments of PS II, and we have successfully completed our first run. We commissioned a novel reflection zone-plate spectrometer and collected Mn L-edge spectra at room temperature from high valent Mn complexes, and preliminary data from PS II. Over the next year, we plan to collect Mn L-edge spectra from the entire Kok cycle and particularly the transient states between the S_3 and S_0 states, where the O-O formation occurs. These time-resolved structural and spectroscopic studies will lead towards a complete understanding of the mechanism of photosynthetic water-oxidation and oxygen evolution.

Functional Models of Photosynthetic Light Harvesting Systems Templated by Self-Assembling Proteins

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Funding:	$596,000

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 2012 HIGHLIGHTS

During the first fiscal year of this project, we have generated new protein scaffolds for chromophore positioning, and we have developed a series of rigid bioconjugation linking groups designed to control the angles with which the chromophores are displayed relative to one another. New water-soluble porphyrins and phthalocyanines have also been synthesized for protein attachment. Initial computational efforts have begun, as have our first time-resolved spectroscopic measurements of the protein-templated light harvesting systems.

The Regulation of Photosynthetic Light Harvesting

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Funding:	$600,000

PROGRAM SCOPE

This project focuses on the regulation of photosynthetic light harvesting and the roles of light-harvesting complex (LHC) proteins and carotenoid molecules. A combination of molecular genetics, femtosecond spectroscopy, and modeling is used to study the mechanisms of non-photochemical quenching (NPQ). In particular, we aim to elucidate the biophysical mechanism of different NPQ components (qE and qI) and the roles of the Photosystem II proteins PsbS and LHCSR in plants and eukaryotic algae, respectively.

FY 2012 HIGHLIGHTS

To gain more detailed insight into the origins of the various NPQ processes and their timescales, we developed a new apparatus capable of measuring the picosecond fluorescence lifetimes during induction of NPQ. In *Chlamydomonas reinhardtii*, we found two short fluorescence lifetimes (65 ps and 305 ps) that appeared with different time constants after high light was turned on, suggesting that they arise from different physical/biochemical processes. We performed site-directed mutagenesis of LHCSR3 to identify amino acid residues that are important for the qE component of NPQ in *C. reinhardtii* and for pH-dependent transient absorption differences *in vitro*. To elucidate the pathways involved in NPQ in other algae, we screened *npq* mutants of *Chromochloris zofingiensis* and *Nannochloropsis oceanica* using chlorophyll fluorescence video imaging. Preliminary analyses of the *C. zofingiensis* mutants showed that some may have deficient levels of LHCSR proteins. Through a genetic screen in *Arabidopsis thaliana*, we identified a thylakoid-associated, thioredoxin-like protein that is involved in qI.

Photobiohybrid Solar Fuels

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Funding:	$900,000

PROGRAM SCOPE

Photosynthesis provides a template for solar energy conversion, and the design of light-harvesting and energy-transducing molecules for solar-fuel production. Reaction steps in photosynthesis are catalyzed by enzymes, which interface with electron-transfer chains to form biochemical networks for energy conversion. The molecular interactions that mediate electron-exchange help to minimize energy costs. Likewise, enzymes operate at or near thermodynamic exchange potentials with substrate specificity and fast turnover, yet the diffusion-controlled reactions within redox transfer chains place limits on overall pathway flux.

The objective of this project is to address the limitations of photosynthesis by developing molecular structures for direct solar conversion. Research aims include characterizing molecular interfaces, light harvesting, energy transduction, and catalysis in natural and photobiohybrid systems for solar H_2 production that are organized into the following approaches: (1) development of computational and theoretical models to understand electron-transfer mechanisms, and enzymatic H_2 activation in [FeFe]-hydrogenases; (2) characterization of self-assembly, photochemical conversion and charge-transfer interfaces in natural and photobiohybrid complexes; (3) electrochemical studies of native and structurally minimized enzymes by electrochemical-scanning tunneling microscopy (STM); and (4) exploration of [FeFe]-hydrogenase structural diversity using crystallographic and biophysical techniques. The long-term impact will be to understand the parameters controlling allocation of light absorption among productive and non-productive processes, the molecular interfaces and control of photochemistry, and how metalloenzymes convert photochemical energy into H_2.

FY 2012 HIGHLIGHTS

A quantum chemical [FeFe]-hydrogenase model encompassing the H-cluster, accessory [4Fe4S]-clusters, and surrounding protein was constructed. Custom computational methods allow for breaking the spin symmetry within accessory [4Fe4S]-clusters, and integration of the initial gas-phase calculation into a QM/MM model of the [FeFe]-hydrogenase H-cluster. In addition, the free energies along proton-transfer pathways were investigated using QM/MM and umbrella sampling techniques. Residues participating in transfer steps were identified and pK_a values for proton exchange were estimated using a thermodynamics integration method.

[FeFe]-hydrogenase was adsorbed onto Au electrodes bearing self-assembled thiol-based monolayers (SAMs). Single-molecule images were obtained in an electrochemical STM that showed tunneling currents increased under an applied bias. A lower limit for k_{cat} of 20,000 s^{-1} (H_2 evolution) was estimated at an overpotential of ~150 mV by normalization of macroscopic voltammetry measurements to enzyme coverage. Assemblies of [FeFe]-hydrogenase with mercaptopropionic acid (MPA) capped CdS nanorods were formed. Kinetics showed that nanorod adsorption competed with ferredoxin binding, presumably to the distal [4Fe-4S]-cluster surface of hydrogenase. Rates of H_2 evolution were proportional to light intensity and donor concentration, with quantum yields (450 nm) of 20%. Time-resolved vibrational spectra of the CdS-hydrogenase complexes by rapid scan FTIR under illumination allowed for detection of electron-transfer to the hydrogenase catalytic site at ms timescales. Development of this technique will provide a window into the structural transitions of hydrogenases under turnover conditions.

Photobiological and Photobiohybrid Solar Fuels Program—Photobiology Project

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Funding:	$450,000

PROGRAM SCOPE

The overarching goal of the photobiology project under the Photobiological and Photobiohybrid Solar Fuels Program is to investigate the regulation of photosynthetic reductant partitioning between H_2 evolution, biomass, and other storage molecules that accumulate under different stress conditions. The objective is to understand the interplay between stress sensing, signal transduction, and transcriptional regulation of specific genes that determine the fate of photosynthetic reductant. This, in turn, will allow one to manipulate and change the metabolic state of the cells under controlled conditions. We are particularly interested in the mechanism of the interaction between different signal/sensor and sensor/transducer molecules, and the complex networks between different signal and the expression of specific genes at the mechanistic level. This project consists of two subtasks that address, respectively, (1) factors required for the regulation of photosynthetic reductant partitioning between CO_2 fixation and H_2 production under anaerobic conditions, and (2) factors required for regulation of reductant and carbon partitioning between biomass and carbon storage molecules under N and other stresses.

FY 2012 HIGHLIGHTS

Subtask A: (1) Insertional mutants previously identified as unable to photoproduce H_2 have been back-crossed and re-screened for O_2 evolution and H_2 production activities. One of them, encoding a gene annotated as involved in transcriptional regulation by anoxia, is being further characterized. (2) A novel transcriptional factor, identified in anaerobically-induced nuclear extracts, was shown by pull-down assays to interact specifically with both HYDA1 and HYDA2. This represents the first identification of a factor specifically regulating hydrogenase gene expression; its interacting partners are being investigated. (3) A manuscript describing the role of FXL1 and FXL5 in binding heme and thus in O_2-sensing was published in *FEBS Letters* (Narayana Murthy, U.M. et al., http://dx.doi.org/10.1016/j.febslet.2012.06.052).

Subtask B: A Synechocystis 6803 mutant that was engineered to be unable to synthesize glycogen, a major carbon storage compound, was employed as a model for the study of carbon partitioning. Under N starvation, the mutant continued photosynthesis but could not grow its biomass. Instead, carbon flux was redirected to the synthesis of pyruvate and alpha ketoglutarate, leading to accumulation of these keto acids in the medium. This discovery represents the first demonstration of photo-catalytic conversion of CO_2 to excreted organic compounds. A paper describing this discovery was published (Damian Carrieri et al 2012 *Energy Environ. Sci.* 5: 9457-9461), and was promoted by Royal Chemical Society as “Hot paper.” A U.S. patent was filed on photosynthetic conversion of CO_2 to the keto acids.

Physical Biosciences

Institutions Receiving Grants

Utilization of Protein Film Electrochemistry to Characterize the Mechanisms Imparting Aerotolerance and Bidirectionality in Solube, Multimeric [NiFe]-Hydrogenases

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Funding:	$150,000

PROGRAM SCOPE

The overall goal of this research is to better understand how structural features control functional aspects of an important class of enzymes called soluble [NiFe]-hydrogenases. These enzymes mediate a reversible two-electron reduction of protons to form hydrogen gas. Studies of these enzymes may lead to improvements in bio-hydrogen production/utilization. Additionally, they serve as models for more complex multielectron redox enzymes such as those involved in nitrogen and carbon dioxide reduction. Two properties of [NiFe]-hydrogenases relevant to energy applications will be investigated: (1) *What structural features influence the catalytic bias of the enzyme?* (2) *What structural features determine the susceptibility of these enzymes to inactivation by molecular oxygen?* [NiFe]-hydrogenases with a broad range of activities will be isolated from biologically diverse sources and characterized using a technique called protein film electrochemistry. Structural variants of these enzymes with precisely targeted changes will also be generated, characterized, and compared with the results for the wild type enzymes to address the two questions above. The comprehensive understanding of the structural features controlling catalytic properties that result from this research can guide the development of improved redox enzymes and/or other novel bio-inspired catalysts.

FY 2012 HIGHLIGHTS

We have successfully characterized at room temperature the electrocatalytic activity of the soluble hydrogenase I (SHI) from *Pyrococcus furiosus* and shown that it has some oxygen tolerance. Preliminary experiments up to 60°C have also been undertaken to understand the temperature dependence of activity in an enzyme from a hyperthermophilic source. A mutant in which the diaphorase subunits have been genetically removed has also be characterized and shown to have a different catalytic bias despite the conserved active site. Solution assays have been designed to facilitate purification of additional proteins from other target organisms, and growth of these microbes is underway.

Calcium-Mediated Regulation of Proton-Coupled Sodium Transport

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Funding: $70,000

PROGRAM SCOPE

Currents of ions passing from one side of the membrane to the other link metabolism to work and play a major role in energy capture. Our goal has been to understand the control of cellular energy transduction through regulation of proteins (secondary active transporters) that couple ion transport to these transmembrane energy gradients. Calcium sensors are emerging as critical regulators of these secondary active transporters.

The Arabidopsis CALCINEURIN B-LIKE10 (CBL10) calcium sensor plays a critical role in the control of sodium ion homeostasis by regulating the activity of the SALT-OVERLY-SENSITIVE1 (SOS1) Na^+/H^+ exchanger. During vegetative growth in salt, CBL10 functions in the removal of cytosolic sodium by interacting with and activating the SOS2 protein kinase which, in turn, phosphorylates the SOS1 Na^+/H^+ exchanger. Our recent studies have shown that alternative splicing of CBL10 generates two major variants with antagonistic functions that contribute to the response to salt. Data supporting this conclusion shows that (1) both CBL10 and CBL10LA are present when plants are grown without salt, (2) levels of CBL10LA are reduced during seedling growth in salt, (3) CBL10 alone is required to activate responses to salt, and (4) CBL10LA must be removed for a salt response to be turned on. Reduction in *CBL10LA* levels during plant growth in salt could generate regulated responses to specific growth conditions. For example, if full activation of SOS1 is not necessary or beneficial during growth in low levels of or transient exposure to salt, CBL10LA could be used to modulate SOS1 activity. During growth in high levels of or prolonged exposures to salt, CBL10LA levels are reduced leading to increased SOS1 Na^+/H^+ exchange. Our current goals are to link alternative splicing of CBL10 to SOS1 activity and to identify the mechanism underlying this interaction. To link alternative splicing of *CBL10* to SOS1 activity, we are asking two questions: (1) *Does CBL10LA keep SOS1 activity off in control conditions?* (2) *Does reduction of CBL10LA in plants grown with salt lead to increases in SOS1 activity?* To identify the mechanisms underlying CBL10 regulation of SOS1 activity, we are investigating three potential points of regulation: (1) CBL10 binding to SOS2 (*in planta* and *in vitro* co-immunoprecipitation assays), (2) CBL10-SOS2 target phosphorylation (interactions assays with recombinant protein and *in vitro* kinase assays), and (3) direct CBL10 regulation of SOS1 (comparisons of SOS1 Na^+/H^+ exchange activity in wild-type vesicles left untreated or treated with CBL10 or CBL10LA protein).

FY 2012 HIGHLIGHTS

We have determined the relative expression patterns and levels of CBL10 and CBL10LA in plants grown with and without salt demonstrated that CBL10 alone is required to activate responses to salt, and that CBL10LA must be removed for a response to salt. In the next period, we use this information to identify the mechanisms underlying CBL10 regulation of SOS1 activity.

Osmoregulation in Methanogens

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

PROGRAM SCOPE

This project aims to categorize the solutes synthesized in archaea and related bacterial hyperthermophiles in response to osmotic and thermal stress, and then to explore any specific interactions of these solutes with macromolecules. There are three specific goals:

(1) Continue to characterize the enzymes in di-inositol-1,2-phosphate (DIP) biosynthesis (inositol-1-phosphate synthase (IPS), inositol monophosphate:cytidine triphosphate cytidylytransferase (IMP-CTase), the membrane-localized 3-phospho-DIP synthase (P-DIPS), and the inositol monophosphate /fructose bisphosphatase (IMPase) that generates DIP as a step to understanding what regulates DIP accumulation.

(2) Explore transcription of the genes in *T. maritima* that are involved in synthesizing DIP.

(3) Use high-resolution NMR field cycling and spin labeled *A. fulgidus* IMPase to look for weak binding sites of osmolytes as a way of exploring specificity in osmolytes thermostabilization.

FY 2012 HIGHLIGHTS

Work towards the first goal includes the crystal structure of the *T. maritima* IMP-CTase, a soluble protein that must transiently associate with its membrane-embedded partner P-DIPS. The structure shows a conserved motif of sugar nucleotide transferases with an interesting modification where the C-terminal cysteine is linked via disulfide to the core of the protein. Refinement is continuing to address the mechanism for this transferase and to explore regions that must interact with P-DIPS.

The last of the specific goals received the most emphasis in 2012 (in part because high-resolution field cycling is a novel technique). Field cycling observing ^{13}C (labeled carbonyls of amino acids) or ^{31}P (diglycerol phosphate) is used to characterize how small molecule interact with an archaeal IMPase whose thermostability we can modulate. By pairing a large excess of small molecules with spin-labeled proteins, we measure their weak binding (up to K_d ~150 mM) to the IMPase and locate the specific binding sites. The results of this aspect of the work should help to provide a molecular picture for osmolyte specificity when it is observed. More importantly, the methodology is robust and useful for a wide variety of systems where one wants to explore weak binding of ligands to macromolecules.

Trafficking to the Protein Storage Vacuoles in Plants

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Funding:	$185,000

PROGRAM SCOPE

The accumulation and mobilization of carbohydrates and storage proteins in plant vacuoles provide a general source of metabolic energy for starch synthesis, regulate the deposition of cell wall components, and have important economic and nutritional significance for humans. We are analyzing different aspects of this process in plants, including their regulatory mechanisms, associated machineries, and accumulated proteins and metabolites. This will provide a deeper understanding of the organizational principles controlling energy mobilization in biological storage systems. To obtain mechanistic information of these complex processes, we are using an integrated systems biology approach that combines computational tools from the physical sciences, analytical tools from the chemical sciences, and a set of cell biological tools from the biochemistry, molecular biology, and cell biology fields.

We believe that the application of our multidisciplinary approach and long-term goals fits well into the DOE Physical Biosciences program and will increase our understanding of the biology of plant vacuoles. This knowledge will greatly contribute to the development of technologies for more efficient generation of biomass as a renewal energy source, and will also provide essential tools to manipulate the energetic yield of plant systems as we unravel the elements required for loading metabolites and proteins of interest into the plant vacuole.

FY 2012 HIGHLIGHTS

The ribosomal protein RPL4A is an important element for the sorting of vacuolar cargoes in a process regulated by auxins. We have identified upstream open reading frames (ORFs) in the 5’-leader sequences of specific mRNAs that modulate the translation of downstream ORFs encoding major gene products. In Arabidopsis, the translational control of auxin response factors (ARFs) by upstream ORFs has been proposed as a regulatory mechanism required to respond properly to complex auxin-signaling inputs. In this study, we identify and characterize the aberrant auxin responses in specific ribosomal protein mutants in which multiple ARF transcription factors are simultaneously repressed at the translational level. This characteristic lends itself to the use of these mutants as genetic tools to bypass the genetic redundancy among members of the ARF family in Arabidopsis. Using this approach, we were able to assign unique functions for ARF2, ARF3, and ARF6 in plant development. This knowledge will provide essential tools to manipulate the energetic yield of plant systems as we unravel the elements required for loading metabolites and proteins of interest into the plant vacuole.

Molecular and Genetic Basis of Sodium and Potassium Transport and Distribution in Plants

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Funding:	$173,874

PROGRAM SCOPE

Salinity stress is progressively causing reduced plant growth, and biomass production in irrigated lands and in natural saline soils causes dramatic reductions in plant biomass production and is detrimental to photosynthetic activity. Salinization of soils has become a major and increasing concern. Our DOE-supported research has shown that the AtHKT1;1 transporter mediates 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 in several labs, 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 and characterized 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, many of the transporters, including the molecular K^+ transport mechanisms across chloroplast membranes, remain unknown. Our research will identify and characterize chloroplast-targeted K^+ transporters and determine their roles in plant growth, chloroplast function, and salinity responses.

FY 2012 HIGHLIGHTS

Our DOE-supported research has led to the model that AtHKT1;1 unloads sodium directly from xylem vessels to xylem parenchyma cells. However, direct comparative *in vivo* electrophysiological analyses of a plant HKT transporter in wild-type and *hkt* loss-of-function mutants had not yet been analyzed. GFP-labeled root stelar cells were used to investigate AtHKT1;1-dependent ion transport properties using patch clamp electrophysiology. This research directly shows that AtHKT1;1 mediates Nernstian Na^+ channel-like currents. Removal of extracellular Na^+ caused regulation of AtHKT1;1-mediated activity in Arabidopsis root stelar cells. The mechanisms controlling xylem parenchyma-specific and sodium - dependent expression of class I HKT transporters are essential for salinity tolerance but remain unknown. We have developed reporter screens to identify metal stress-induced gene expression mechanisms. This research is identifying the regulation mechanisms that function in controlling *AHKT1;1* expression and Na^+ tolerance in plants.

The mechanisms mediating salinity stress-induced chlorosis and the genes encoding for K^+ uptake or release from chloroplasts remain unknown. Our recent research has led to identification of candidate chloroplast cation transporters that are essential to chloroplast function. We have found that isolated mutant plants in candidate chloroplast cation transporters show dramatically impaired growth and reduced photosynthetic activity and altered salt sensitivity. These transporters are being biochemically and biophysically characterized and their physiological relevance and roles in salinity stress elucidated *in planta*.

Proteomic Study of Brassinosteroid Responses in Arabidopsis

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Funding:	$160,000

PROGRAM SCOPE

The goal of this project is to understand the molecular and biochemical mechanisms through which brassinosteroid regulates gene expression and plant growth and development. Brassinosteroid is a major growth-promoting hormone that controls a wide range of developmental and physiological processes in plants and has a major effect on biomass productivity. Understanding the molecular circuit through which brassinosteroid controls cellular processes is important for developing efficient bioenergy systems. Our strategy to achieve this goal is to first use cutting-edge analytical tools, such as mass spectrometry, to identify proteins, protein-protein interactions, and protein modifications that are affected by the brassinosteroid signal; and then study the functions of the identified proteins and their action mechanisms using combinations of molecular, genetic, and biochemical approaches. Our previous studies have identified several important proteins that mediate brassinosteroid signal transduction. The specific aims of this project include (1) illustrate the functions of a brassinosteroid-regulated nuclear protein that controls the transition from vegetative to reproductive development in Arabidopsis and (2) identify additional brassinosteroid-regulated nuclear proteins and dissect their functions in regulation gene expression and plant growth.

FY 2012 HIGHLIGHTS

We have confirmed that brassinosteroid induces dephosphorylation of the ARB1 protein (previously named NBR1) and that ARB1 promotes flowering. We have purified the ARB1 protein complex and analyzed it using mass spectrometry. We identified 22 *in vivo* phosphorylation sites of ARB1 and showed that 9 of these sites were phosphorylated by the BIN2/GSK3 kinase *in vitro*. We identified 80 putative ARB1-associated proteins; 52 of these are involved in RNA metabolism (RNA binding, splicing, or RNA processing) and some of them are involved in RNA-directed DNA methylation. Several of the ARB1-associated proteins have been reported to affect flowering. Our results provide strong evidence for a new branch of the brassinosteroid signaling pathway that mediates brassinosteroid regulation of RNA processing and the transition from vegetative to reproductive growth. In the next period, we will identify the RNAs directly affected by ARB1 and determine the effects of phosphorylation sites on ARB1 activity. These experiments will elucidate the molecular mechanism underlying the function of ARB1 in brassinosteroid regulation of plant flowering.

Genetic and Biochemical Analysis of Xyloglucan Galactosylation in Arabidopsis

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

PROGRAM SCOPE

Our research objectives are to determine the rate-limiting steps in galactose attachment to the backbone of the hemicellulose xyloglucan. The main experimental approaches are as follows: (1) increase the availability of the predicted donor substrate UDP-galactose by overexpressing UDP-glucose 4-epimerase in the cytosol or the endomembrane system of Arabidopsis plants, (2) characterize the biochemical properties of known or predicted xyloglucan galactosyltransferases from Arabidopsis by recombinant expression of the respective proteins in *Pichia pastoris* followed by enzyme assays with a variety of acceptor substrates, and (3) overexpress these proteins in Arabidopsis either individually or in combination under the control of a strong constitutive promoter. Xyloglucan from the transgenic lines will then be analyzed for changes in the degree of galactosylation by mass spectrometry and NMR of enzymatically generated oligosaccharides. We hope that this approach will provide insights into the mechanisms by which monosaccharides from nucleotide sugars are allocated to the synthesis of specific cell wall components. Furthermore, the transgenic plants may display interesting changes in cell wall properties since structural changes in xyloglucan are expected to affect the mechanical strength of xyloglucan-cellulose interactions.

FY 2012 HIGHLIGHTS

(1) The putative galactosyltransferase MUR12 was shown to transfer radiolabeled galactose from UDP-galactose to specific xylose residues in the seed storage xyloglucan from *Hymenaea courbaril*. Considering that the recombinant protein was obtained in a yeast expression system, the enzyme clearly acted as a *bona fide* galactosyltransferase without the need for plant-derived cofactors. Somewhat surprisingly, the MUR12 protein converted XXLG subunits to XLLG but did not produce XLXG from XXXG. In enzyme assays conducted in parallel to those described above, recombinant MUR3 protein converted XXXG to XXLG but did not convert XLXG to XLLG. Both MUR3 and MUR12 used the *Hymenaea*-specific building block XXXXG as an acceptor substrate with the formation of XXXLG and XLXXG, respectively.

(2) Subcellular localization studies demonstrated targeting of both MUR3 and MUR12 to the Golgi; however, co-localization of the two proteins was partial rather than complete.

(3) Homozygous Arabidopsis plants overexpressing both MUR3 and MUR12 were generated from previously characterized lines, and are now ready for analysis of their xyloglucan structure.

From the Soil to the Seed: Metal Transport in Arabidopsis

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

PROGRAM SCOPE

Deficiencies of micronutrients, such as Fe and Zn, commonly limit plant growth and crop yields. The long-term goal of our program is to understand how plants acquire metal micronutrients from the soil and distribute them throughout while protecting themselves from the potential damage metals can cause to living tissues. Our studies are helping to illuminate how to improve seedling growth in soils with limited micronutrient availability. Our lab has previously identified the major Fe transporter responsible for Fe uptake from the soil, IRT1, a founding member of the ZIP family of metal transporters. Arabidopsis is predicted to have 16 *ZIP* genes, and we are systematically characterizing all the family members. In addition to the ZIP transporters, we are also exploring the function of an Fe and Mn transporter, VIT1, that localizes to the vacuolar membrane. We are particularly interested in determining how various ZIP transporters and VIT1 influence the metal content of the seed.

FY 2012 HIGHLIGHTS

We have been awarded beam time at three different DOE-supported facilities—the National Synchrotron Light Source at Brookhaven National Lab, the Advanced Photon Source at Argonne National Lab, and the Stanford Synchrotron Radiation Lightsource—and are continuing to examine metal distribution using synchrotron x-ray fluorescence microscopy (sXRF). Most recently, we have focused our attention on Mn, an essential trace element present in PSII as a polynuclear cluster that catalyzes the water splitting reaction. In addition to being a cofactor for a variety of enzymes (including various decarboxylases of the TCA cycle, RNA polymerases, and numerous glycosyl transferases), Mn is a constituent of Mn superoxide dismutase, the principal antioxidant enzyme of mitochondria. We had previously demonstrated that Mn is localized in the sub-epidermal cell layer of the embryonic cotyledons. By imaging developing seedlings, we have shown that this pool of Mn is quickly re-distributed in young cotyledons. We are also imaging various lines with defects in vacuolar metal storage and have determined that the inability to retrieve metals from the vacuole has more severe consequences for seedling development than an inability to store metals in the vacuole in the first place. To identify other genes involved in Mn homeostasis, we are screening Arabidopsis accessions via ICP-MS and xSRF, looking for accessions with either altered concentrations and/or localization of Mn. We have completed the elemental profile of 348 Arabidopsis accessions by ICP-MS and see a range of 64 µg g-1 to 160 µg g-1 Mn for shoot tissues. We can also use seed data to identify responsible loci; for seed, we see a broad range of 30.8 µg g-1 Mo to 128.4 µg g-1 Mo.

Post-Transcriptional Regulation of Ethylene Perception and Signaling in Arabidopsis

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Funding:	$70,000

PROGRAM SCOPE

The simple gas ethylene functions as an endogenous regulator of plant growth and development. Ethylene is perceived in the plant Arabidopsis by a five-member family of receptors related to bacterial histidine kinases. Our data support a general model in which the receptors exist as parts of larger protein complexes. Our recent goals have been to identify components of these receptor complexes and to determine the roles that physical interactions among components of the complex play in signaling. To this end, we have characterized interactions between the ethylene receptors and the Raf-like kinase CTR1, our data indicating that the level of CTR1 is dynamically regulated due to ethylene-induced changes in receptor levels. We are also characterizing a new class of regulators we refer to as Ethylene Feedback Mediators (EFMs) because they are transcriptionally induced by ethylene and negatively regulate the signaling pathway. Localization to the endoplasmic reticulum and bimolecular fluorescence complementation analysis (BiFC) support an interaction with and potential regulation of signal output from the ethylene receptors. We are also interested in determining the role of histidine kinase activity in signaling by the receptors, and how it may affect interactions among components of the receptor complex. For this work, we have been taking a genetic approach, characterizing plant lines in which kinase-inactive versions of the receptor ETR1 have been introduced. Physiological and molecular analyses on these lines indicate that histidine-kinase activity is not required for signaling but plays a modulating role in the regulation of ethylene responses. Taken together, our studies suggest that the tremendous range of ethylene receptor signaling capacity is achieved in part by incorporating a variety of regulatory mechanisms.

FY 2012 HIGHLIGHTS

(1) We have identified several effects of receptor histidine-kinase activity on their signal output, including effects on the protein levels of CTR1 and on signaling through a two-component phosphorelay to mediate a subset of the plant responses to ethylene. These results indicate that the receptors employ multiple signaling pathways to regulate their diversity of downstream effects.

(2) To facilitate characterization of the EFMs, we generated overexpression lines and higher order mutant combinations. Characterization of these lines indicates that the EFMs could serve as key factors in regulating the ability of plants to adapt to changes in ethylene concentration.

(3) We have determined that ethylene receptors play a significant role in regulating cell division in Arabidopsis along with their more generally known role in regulating cell expansion, the negative effect on cell division thus serving as a partial explanation for the effects of ethylene on plant biomass.

Engineering Intelligent Scaffolds by Supramolecular Self-Assembly

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PROGRAM SCOPE

Synthetic polymers surround us, from the vehicles we use to the houses we live in, from the clothes we wear to the electronics that entertain us. Despite this abundance of synthetic polymers, we have yet to approach the complexity, Ångström level precision, or programmability that is encoded in the primary sequence of biopolymers that Nature employs and exemplifies in the living cell. In this regard, we have developed methods to characterize self-assembled peptide structures across length scales from Ångströms to microns. These methods, and the structural insight they provide, have empowered confidence in our ability to engineer new assemblies and discover the orthogonal elements necessary for the construction of a basic supramolecular assembly toolbox. In this context, our goal is to create peptidic self-assembled systems that have function—specifically, breaking/making bonds by engineering assemblies in which we have exquisite control of chemical functionality displayed on the surface(s). This is an essential step towards creating materials that can adapt in response to environmental pressure, and thereby learn from their experiences, which can be considered materials or networks with intelligence. Intelligent behavior may be an inherent property of matter, and we propose that it is now possible to lay the foundations for the discovery of intelligent materials in a synthetic network.

FY 2012 HIGHLIGHTS

Nanoscale patterned surfaces represent a key architectural element in our long-range plans for developing functional materials. Covalent attachment of the fluorescent molecule rhodamine (Rh) to the end of the peptide KLVFFAE allows us to follow assembly of Rh-LVFFAE/KLVFFAE into peptide nanotubes with fluorescence microscopy. Spatial characterization with fluorescence lifetime imaging microscopy detects distinct transitions in the lifetime along the length of the tube. These nanotubes represent the first patterned assembly of peptide nanotubes, which we now need to explore the dynamic, structural, and photochemical properties.

Ubiquitin-Like Proteins in Protein Conjugation and Sulfur Transfer in Archaea

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PROGRAM SCOPE

Archaea are microorganisms that are distinct from bacteria and have tremendous potential to advance DOE missions toward a bio-based economy. Archaea are central to global inorganic and organic cycles (e.g., methanogenesis) and contribute to a large fraction of Earth's biomass. Archaea are ideal for biocatalyst development encoding enzymes that are stable and active in the harsh conditions encountered in industrial processes (e.g., high temperatures, high/low pH, high solvent) and are not pathogens. Archaea also provide new insight into metabolic biochemistry and biological diversity with as much as 50% of their genes encoding novel proteins with no obvious counterparts in the other domains of life.

Our long-term goal is to understand how proteins are targeted to proteasomes for degradation and determine what pathways are regulated by this type of post-transcriptional mechanism in archaea. Investigating archaeal proteasomes and their associated targeting mechanisms is important in furthering our understanding of this unusual group of organisms and in advancing our ability to modify metabolic pathways for applications in biotechnology (e.g., targeting proteins for post-translational modification, modulating protein stability/activity, altering protein partners).

FY 2012 HIGHLIGHTS

Recently, we discovered that archaeal ubiquitin-like (Ubl) proteins (named SAMPs) are covalently attached to protein targets. This process (sampylation) has deep evolutionary roots with ubiquitylation, a pathway that targets proteins for proteasome-mediated proteolysis in eukaryotes. An archaeal ubiquitin (Ub)-activating E1 enzyme homolog (named UbaA) was found to be required for sampylation, and SAMPs were found conjugated to protein targets through isopeptide bonds between the alpha-carboxyl group of the C-terminal glycine residue of the SAMP and the epsilon-amino group of lysine residues of target proteins. Target proteins and sites of sampylation were diverse with targets including homologs of sulfur mobilization, transcription, stress response, and other functions. Tandem-based affinity labeling and purification of select target proteins confirmed their sampylation and established a basis for elucidating the biological function of SAMP modification in archaeal cells. An archaeal JAMM (JAB1/MPN/Mov34 metalloenzyme) peptidase (HvJAMM1) was found to cleave the isopeptide bond formed between SAMPs and their protein targets, providing evidence that sampylation is reversible. Sampylation was also found functional in archaea of the phyla Euryarchaeota and Crenarchaeota, revealing the system is relatively universal among the Archaea domain. Components of the sampylation system also mediate sulfur transfer based on our finding that they are required for tRNA thiolation and dimethylsulfoxide reductase activity in the archaeon *Haloferax volcanii*. Overall, our work reveals a universal system of protein conjugation in archaea that shares biochemical features with eukaryotic ubiquitylation, thus providing a fundamental insight into the diversity of Ubl systems in living cells.

Cell-Type Specific Hemicellulose Structures in the Root Cell Walls of Arabidopsis and Brachypodium

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Funding:	$170,000

PROGRAM SCOPE

Roots have diverse biological functions, including the uptake of water and nutrients from the environment and the interaction of the plant with soil microbes, that are critical for the adaptation and survival of vascular plants. Roots also constitute a major component of the biological carbon cycle due to the large amounts of fixed carbon that they sequester. A significant proportion of the carbon in roots is contained in cell walls, whose predominant components are polysaccharides and lignin. Despite their clear biological importance, root cell walls have not been studied as extensively as cell walls from aerial tissues. This lack of knowledge constitutes a major impediment to understanding the biology of plant growth.

Hemicelluloses, which include xyloglucans and xylans, constitute an important class of developmentally regulated cell wall polysaccharides. We hypothesize that variations in the structures of these polymers lead to cell-specific differences in the biophysical properties of the cell wall, enabling each different cell type to perform a distinctive set of biological functions. This research is designed to test and extend our hypothesis by combining genetic, structural, and sensitive immunocytochemical analysis to identify and characterize cell-specific structural features of hemicellulosic polysaccharides in the roots of two model plants, *Arabidopsis* and *Brachypodium*. Achievement of this goal will provide a deeper understanding of the biophysical mechanisms by which the roots of vascular plants develop and adapt to environmental variations. Such knowledge is critical for the rational development of plant lines with root systems that are optimized to achieve specific agronomic goals such as drought tolerance and improved growth in nutrient-depleted soils.

Center for Plant and Microbial Complex Carbohydrates

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Funding:	$822,571

PROGRAM SCOPE

The Complex Carbohydrate Research Center (CCRC) of the University of Georgia is a national resource for the study of complex carbohydrates. The CCRC provides services and training to academic, government, and industrial researchers who study the complex carbohydrates of plants and microbes by supporting 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 biomedical glycobiology, vaccine development, and biomass conversion to biofuels is being recognized.

The CCRC provides several "high demand" analytical services to the scientific community, including (1) purification and analysis of plant and microbial polysaccharides; (2) purification and characterization of plant and microbial glycoproteins; (3) molecular weight determination by SEC, MALDI-MS, or ESI-MS; (4) glycosyl composition analysis: GC-MS and HPAEC; (5) glycosyl linkage analysis; (6) determination of absolute configuration; (7) structural characterization by mass spectrometry [ESI-MS and ESI-MS/MS, MALDI-MS and MALDI-MS/MS, online liquid chromatography electrospray ionization mass spectrometry (LC-ESI-MS/MS)]; (8) 1-D and 2-D NMR spectroscopy; (9) Lignin analysis using Py-MBMS and Py-GC-MS; and (10) CarboSource Services: production and distribution of rare nucleotide-sugars, acceptors required for polysaccharide and glycoconjugate biosynthesis, and of monoclonal antibodies reactive against plant cell wall epitopes.

In the fall 2012, the CCRC will incorporate several new services, which include (1) developing new improved reduction steps for the linkage analysis of uronic acid-containing oligo- and polysaccharides, (2) expanding lignin and tannin analysis by Py-MBMS and Py-GC-MS, (3) reducing end analysis of polysaccharides, and (4) performing glycome profile analysis.

Training students and scientists in various fields of carbohydrate science is a very important part of the CCRC’s mission. Training occurs when undergraduate students, graduate students, postdoctoral fellows, and visiting scientists undertake research projects with or take formal courses from CCRC 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 institutions, government laboratories, and private industry.

Hypothermophilic Multiprotein Complexes and Pathways for Energy Conservation and Catalysis

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Funding:	$200,000

PROGRAM SCOPE

We are investigating the properties and mechanisms of assembly 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 novel protein complexes under study have the remarkable property of being synthesized (self-assembling) at temperatures near 100°C in a so-called hyperthermophilic microorganism. 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 for this work is *Pyrococcus furiosus* (Pf), which grows optimally at 100°C. Pf obtains carbon and 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 production by a ferredoxin-dependent, membrane-bound hydrogenase (MBH) to ion translocation and 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 the synthesis of a membrane complex termed MBX. MBX is highly similar in gene organization to MBH and is proposed to oxidize ferredoxin, reduce S°, and conserve energy by an as yet unknown mechanism. The specific aims of the proposed research are to characterize MBH, MBX, SHI, and minimal forms of SHI and MBH. The results of this research will provide a fundamental understanding of how the metabolism of S° and hydrogen leads to energy conservation (MBH and MBX) in Pf using novel catalytic mechanisms. 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, kinetic, spectroscopic, and genetic techniques. This project also leverages both on-going and new collaborations involving x-ray crystallography.

FY 2012 HIGHLIGHTS

We have engineered Pf to over-produce an affinity-tagged, four-subunit holoenzyme form of SHI and a tagged two-subunit form that directly interacts with a pyruvate-oxidizing enzyme without an intermediate electron carrier. An affinity-tagged version of MBH has also been constructed, but the yield of the detergent-solubilized protein, which apparently contained all 14 subunits, was low. Deletion strains of Pf lacking SHI, MBH, and MBX have been constructed and characterized, along with strains lacking NSR and SipA, two additional enzymes involved in S° metabolism. An extensive phylogenetic and bioinformatic analysis of MBH and MBX revealed that they are modular in nature and represent ancestral respiratory complexes.

Identification and Characterization of Selected Glycosyltransferases Involved in the Synthesis of the Side Chains of the Cell Wall Pectic Polysaccharide Rhamnogalacturonan II

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Funding:	$170,000

PROGRAM SCOPE

Rhamnogalacturonan-II (RG-II) is a complex pectic polysaccharide whose structure is conserved in the primary cell walls of all vascular plants. Cross-linking of RG-II by borate, a plant micronutrient, is known to be required for normal plant growth and development. This has led to the hypothesis that RG-II must be synthesized with the correct structure to interact with borate and thereby regulate the properties of the pectic network and ultimately the cell wall. A genetic approach to identifying the genes and proteins involved in RG-II synthesis has met with limited success as mutations that lead to altered RG-II structure are lethal or result in plants that exhibit abnormal growth. We will use biochemical approaches to test our hypothesis that adding apiose (Api), deoxy-3-octulosonic acid (Kdo), and deoxy-2-heptulosaric acid (Dha) to the galacturonan backbone is controlled and regulates RG-II formation. We have developed methods to enzymically synthesize the nucleotide sugars UDP-Api, CMP-Kdo, and CMP-Dha in amounts sufficient for glycosyltransferases (GTs) activity assays. We will use these nucleotide sugars to identify GT activities that initiate RG-II side chain formation by adding Api, Kdo, and Dha to the galacturonan backbone. Selected enzymes will be purified or enriched by conventional and affinity-based chromatographies and their amino acid sequences (LC-MS-based peptide sequencing) used to identify their corresponding genes. We will also determine if the amounts of RG-II formed are increased by over-expressing UDP-Api synthase in Arabidopsis. These studies will lay the foundation for identifying the remaining molecular components required for RG-II assembly and for developing a greater understanding of RG-IIs role in plant growth and development.

FY 2012 HIGHLIGHTS

This project initiated in August 2012; therefore, there are no highlights to report.

Secondary Wall Formation in Fiber Cells

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Funding:	$185,000

PROGRAM SCOPE

We propose 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-Xyl*p*-(1->3)-alpha-L-Rha*p*-(1->2)-alpha-D-Gal*p*A-(1->4)-D-Xyl*p*. 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. Although genes encoding xylan xylosyltransferases and glucuronyltransferases have recently been characterized biochemically, genes responsible for the biosynthesis of the xylan reducing end sequence, the addition of arabinosyl side chains, and the addition of the acetyl, methyl and ferulate groups have not been enzymatically determined. 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 2012 HIGHLIGHTS

We have discovered that three Arabidopsis DUF579 domain-containing GXM proteins are methyltransferases catalyzing the transfer of the methyl group onto GlcA side chains on xylan. We have shown that the *GXM* genes are expressed in secondary wall-forming cells and their encoded proteins are located in the Golgi. Chemical analysis of single and double *gxm* mutants has revealed that *gxm* mutations cause a loss of methylation of GlcA side chains. Consistent with their roles in methylation of

GlcA side chains on xylan, mutations of *GXM* genes were found to cause a loss of glucuronoxylan methyltransferase activity and recombinant GXM proteins exhibited glucuronoxylan methyltransferase activity. Our results demonstrate that GXMs are methyltransferases responsible for 4-*O*-methylation of GlcA side chains on xylan.

Understanding the Mechanism by which Non-Catalytic Carbohydrate Binding Modules Contribute to Plant Cell Wall Degradation

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A summary for this program was not available at press time.

Genetic Analysis of Hydrogenotrophic Methanogenesis in *Methanosarcina* Species

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Funding:	$185,000

PROGRAM SCOPE

The long-term goal of our research is to expand our knowledge regarding hydrogen-dependent (hydrogenotrophic) methanogenesis by members of the genus *Methanosarcina*. A central aspect of the study is examination of the genotypic and phenotypic differences between *M. barkeri*, an organism that grows well on H_2/CO_2, and *M. acetivorans*, a closely related organism that is incapable of growth on H_2/CO_2. The differences in hydrogen metabolism lie at the center of the energy-conserving electron transport chains of the two organisms. Examination of the molecular, genetic, biochemical, and physiological traits that underpin these differences is expected to deepen our overall understanding of methanogenesis, hydrogen production/consumption, and anaerobic metabolism; all of which are central themes in the DOE Energy Biosciences research program. The specific goals are (1) characterization of energy-conserving electron transport in *M. barkeri* via a proposed hydrogen-cycling mechanism, (2) characterization of hydrogen-independent energy-conserving electron transport in *M. acetivorans*, and (3) assessment of the roles of the multiple heterodisulfide reductase (Hdr) isozymes in *M. barkeri* and *M. acetivorans*.

FY 2012 HIGHLIGHTS

We have made substantial progress in elucidating the genetic and metabolic traits that allow or disallow the use of hydrogen by the two *Methanosarcina* species. Our research shows that *M. barkeri* utilizes H_2 as obligate intermediate during methane production regardless of the growth substrate being used. In this process, H_2 produced in the cytoplasm diffuses out of the cell where it is reoxidized with transfer of electrons into the energy conserving electron transport chain. This “hydrogen cycling” metabolism leads directly to production of a proton motive force that can be used by the cell for ATP synthesis. In contrast, *M. acetivorans* has evolved a hydrogen-independent electron transport chain involving unique energy-conserving steps. We identified two gene clusters, designated *rnf* and *hrdABC*, as potential players in this presumptive electron transport chain. Mutants lacking these genes have substantial defects in growth and methane production consistent with a role in energy-conserving electron transport. Taken together, the data indicate surprising differences in the electron transport chains of these closely related methanogens, which we believe reflect the adaptation to freshwater and marine environments, respectively.

Mechanistic Studies of Catalysis in Quinone Electron Transfer Using High-Resolution EPR

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Funding:	$180,000

PROGRAM SCOPE

Our goal is on use of modern, high-resolution 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 *bc*$_1$ complex, and the Q_H-site of the *bo*$_3$ 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 2012 HIGHLIGHTS

Semiquinone in the Q_H site of cytochrome bo$_3$ ubiquinol oxidase: Selective ^{15}N isotope labeling of the cytochrome *bo*$_3$ ubiquinol oxidase from *E. coli* with auxotrophs was used to characterize the hyperfine (hf) couplings with the side-chain and peptide nitrogens (i.e., potential H-bond donors) from R71, H98, and Q101 residues around the semiquinone (SQ) in the high-affinity Q_H site. The 2D ESEEM have directly identified the $N_{⍰}$ of R71 as an H-bond donor carrying the largest amount of the unpaired spin density. In addition, weaker hf couplings with the side-chain nitrogens from all residues around the SQ were determined. The approach was extended to the virtually inactive D75H mutant, where the intermediate SQ is also stabilized. We found that the N_{ε} from H75 carries most of the unpaired spin density instead of the $N_{⍰}$ of R71, as in the wild-type *bo*$_3$. We utilized density functional theory calculations to model the experimental ^{1}H, ^{15}N and ^{13}C hf couplings for the Q_H site and to describe the protein-substrate interactions in both enzymes. We identified the factors responsible for the asymmetric distribution of the unpaired spin density in the Q_H site and pondered the significance of this asymmetry to the quinone’s electron transfer function.

Semiquinone in Q_A and Q_B site of bacterial reaction center: The H-bond environment around the Q_B site SQ in bacterial reaction center is not indicated by the crystal structure, which shows four potential H-bond donors: HN_δ of His-L190 near carbonyl oxygen O4, Ser-L223 (hydroxyl OH), Ile-L224, and Gly-L225 (both backbone NH) near O1. ^{1}H and ^{14,15}N 2D ESEEM studies supported by QM/MM calculations have shown that (1) His-L190 and Gly-L225 form H-bonds with O4 and O1, respectively; (2) Ile-224 is coupled very weakly with the SQ_B; and (3) no H-bond is formed between Ser-L223 and the SQ_B. Ser-L223 is likely to be H-bonded to the carboxylate group of Asp-L213 after the first flash. The calculations also reproduce a difference in the asymmetry of spin density distribution between SQ_A and SQ_B, in agreement with ^{17}O and ^{13}C couplings of carbonyl groups.

Genetic Analysis of Ca^{2+}-Priming in Arabidopsis Guard Cell Stomatal Closure in Response to the Drought Hormone Abscisic Acid

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Funding:	$57,120

PROGRAM SCOPE

By controlling ionic fluxes across membranes, land plants establish a system of osmotic gradients to control the distribution of water according to its availability. Upon water limitation by draught of increased soil salinity, plants synthesize the stress hormone abscisic acid (ABA). In order to minimize water lost by transpiration, ABA acts on guard cells within the epidermis to decrease their osmotic pressure and close the stomatal pores. Ca^{2+} plays important roles in at least two steps along this signaling pathway. First, prior to ABA biosynthesis, drought or osmotically-stressed plant cells exhibit a rapid cytosolic Ca^{2+} burst. The immediacy of these transients suggests that they are among the earliest mechanisms in the signaling pathway. Second, further downstream of the initial drought-sensing mechanism, ABA induces the gating of guard cell anion channels in a CA^{2+}-dependent manner. However, the mechanisms of CA^{2+} release in guard cells, as well as how Ca^{2+} and other signals are integrated into ion channel activation, remain poorly understood. This research aims to identify and characterize how plants encode and respond to limiting water availability by genetically identifying modulators of these Ca^{2+}-dependent steps.

FY 2012 HIGHLIGHTS

To develop Arabidopsis models that alter Ca^{2+} transients, the PI has taken two approaches. The first is to use knockout plants of CAS, a Ca^{2+} binding chloroplast gene. CAS mutants have been shown to nearly abrogate Ca^{2+} transients in guard cells. The PI has found that the CAS-2 mutant exhibit a “cool” leaf temperature relative to wildtype. Nevertheless, the precise function of CAS remains unclear. His second approach to alter Ca^{2+} transients involves the use of Cax, a $H+/Ca^{2+}$ exchanger whose function in Ca^{2+} regulation is clear. The PI will mutagenize Cas-2 or sCax1 lines and look for enhancers or suppressors of the leaf temperature phenotype. He has screened 2,357 mutant seedlings and selected those with the most divergent Ca^{2+} responses. Thus far, he has obtained 15 lines that show a strong repeatable phenotype. He has begun to map the causative mutations underlying the phenotypes.

The PI has established an independent approach for assessing the ability of plants to sense limiting water. This assay tests the gravitropic versus the hydrotropic response of the root tips. The PI has already found two mutants that show reduced hydrotropism. These mutants are likely to be directly involved in early drought sensation since they have a phenotype in two independent assays. His next step will be to map the causative mutations.

The Role of Carbonic Anhydrase in C(4) Photosynthesis

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Students:	1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$114,240

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 C_4 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 C_4 photosynthesis, the hydration of CO2 into bicarbonate, and is potentially rate limiting in C_4 grasses. Using insertional mutagenesis, we have generated CA mutants in maize; and we 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 C_4 plants. Finally, I propose parallel experiments in Setaria viridis to explore its relevance as model C_4 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 2012 HIGHLIGHTS

By generating knockouts of maize carbonic anhydrase genes, we are able to assay the plant response to limited catalyzation of the first reaction in C_4 photosynthesis. Both physiological measurements to assay CA activity and RNA-seq experiments to explore the network of interactions involved in the beginning steps of C_4 photosynthesis are being used to complete this aim.

Using fluorescently-tagged proteins, the localization of different CA paralogs in maize will be assayed. These results will be used in connection with the results from the first objective to elucidate the role of CA in C_4 photosynthesis.

Experiments using Setaria viridis in parallel with maize are being performed in an effort to validate Setaria as a relevant C_4 grass model. Because experiments in Setaria can be performed at an accelerated rate compared to maize, a more comprehensive understanding of CA cell biology as well as a functional dissection of CA could be achieved if this system proves applicable.

Investigations into the Metabolic Diversity of Microorganisms as Part of Microbial Diversity

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Sr. Investigator(s):	
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Funding:	$30,000

PROGRAM SCOPE

The MBL **m**icrobial **d**iversity **s**ummer **c**ourse provides graduate students, postdoctoral scholars, and established investigators with an unequaled opportunity to explore the microbial diversity of the natural world. The course is an immersive research experience consisting of 6.5 weeks of lectures, laboratory exercises, field work, and individual and group research projects. Foremost investigators from around the world visit the course every summer to participate in course mini-symposia, to lecture, and to interact with students in the laboratory and in the field. In the laboratory, the students learn the latest techniques to cultivate diverse microbes, including organisms involved in bioenergy and the carbon cycle, such as oxygenic and anoxygenic phototrophs, methanogens, and biomass degraders. They then learn molecular biological and other techniques to characterize cultures and microbial communities, including next-generation high-throughput sequencing, metagenomics, bioinformatics, fluorescence in situ hybridization and other advanced microscopy techniques, and single cell techniques such as Nano-SIMS. The lectures and laboratories prepare students to embark on projects the second half of the course. The immersive, integrative, inter-disciplinary, and international nature of the course provides a training opportunity that is currently not available elsewhere in the United States.

FY 2012 HIGHLIGHTS

In 2012, we had another 20 excellent students representing areas as diverse as systems biology and geochemistry. Besides the two directors and three in-house faculty, the students received lectures from 30 prominent scientists, including Penny Chisholm, Norm Pace, Victoria Orphan, Roberto Kolter, Gijs Kuenen, and Dianne Newman. The first minisymposium covered "Microbial Consortia," while the second was on "Microbial Groups Driving Climate Change." While the main goal of the student projects is that they learn new concepts and techniques, some projects do obtain novel results; and four 2012 students will be presenting posters at the 2013 American Society for Microbiology Meeting. As in all years, the student evaluations of the course were stellar, with the term "life-changing" used often. Thus the course has maintained its position as the premiere experience in general microbiology.

Integrating Cation Transport and pH Across Endomembranes with the Secretory System

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Funding: $150,000

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 the 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 are studying a subfamily of predicted cation/H^+ exchangers (CHX) that are present in Spirogyra to higher plants, but rare or absent in metazoan. Studies in yeast and E. coli indicate that CHX members mediate K+ transport, though they are distinct in function from the better-studied NHX1-related members. Arabidopsis CHX20, preferentially expressed in guard cells, is important for stomatal opening, and CHX21 and CHX23 affect the guidance of pollen tubes; however, the biological functions of AtCHX16-19 are ill-defined. Based on localization and mutant analyses, we hypothesize that CHXs modulate 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 plant tissues. To test this idea, we are studying (1) the transport mode of CHX as a channel or exchanger; (2) the regulatory role of hydrophilic carboxyl domain of CHXs on activity, membrane sorting, or both by truncations and point mutations; (3) soluble and membrane interacting partners that are potential regulators and effectors; and (4) the biological role of selected CHX proteins in plant cells. The dynamic endomembrane of plant cells is integral to cytokinesis, cell expansion, defense, cell wall formation, and seed development, thus these studies are directly relevant to the mission of the Department of Energy and to a better understanding of determinants for enhancing plant biomass and plant tolerance to abiotic stress.

FY 2012 HIGHLIGHTS

(1) Based on point mutations, the transport mode of CHX17 in yeast resembles an exchanger; however, its activity in E. coli is like a cation leak channel. (2) The carboxylic tail domain of CHX17 has little to no effect on activity, though truncated forms are mis-sorted indicating a role in protein sorting. (3) Triple and quadruple mutants show reduced seed set, indicating CHX16/17/18/19 have roles in fertilization and/or seed development. Studies to identify potential regulators and effectors are on-going. Next year, we want to identify critical residues needed for CHX17 activity and determine the specific roles of CHX16-19 in plant reproduction.

Cellulose and the Control of Growth Anisotropy

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Funding:	$170,000

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. 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 2012 HIGHLIGHTS

We developed a forward-genetic screen to identify genes affecting root morphology. We mutagenized a wild-type line, bulked up nearly 5,000 M2 families, and have screened them all. For screening, we developed conditions to find temperature-dependent root swelling because constitutive loss-of-function could be lethal. So far, we have bulked up numerous mutants with root swelling, as well as those with other phenotypes, such as no root hairs and root bifurcation. Additionally, through screening natural populations, we have identified a so-called quantitative trait locus (QTL) for root elongation rate. Finally, we have demonstrated that *B. distachyon* genes for cellulose synthesis in the primary cell wall are functionally equivalent to their counterparts in a non-grass species.

Interdisciplinary Research and Training Program in the Plant Sciences

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Students:	17 Postdoctoral Fellow(s), 25 Graduate(s), 22 Undergraduate(s)
Funding:	$3,200,000

PROGRAM SCOPE

The MSU-DOE Plant Research Laboratory (PRL) conducts basic interdisciplinary research on photosynthetic organisms and trains graduate students and postdoctoral researchers in this area of science. Current research conducted by the PRL faculty addresses two integrated themes: (1) interactions of photosynthetic organisms with the environment (He, Howe, Kramer, Montgomery, Thomashow, and Walton); and (2) the biogenesis, biochemistry, and biophysics of cellular energy systems (Brandizzi, Hu, Keegstra, Kramer, Montgomery, and Wolk). The research includes multiple interactive projects aimed at understanding the dynamic regulation of photosynthesis and growth in response to fluctuating environmental conditions. Specific goals include determining the regulatory and structural mechanisms that couple photosynthetic energy capture and growth, acclimation of photosynthesis and growth in response to biotic and abiotic stresses, and the identification of novel genes that contribute to photosynthetic efficiency and robustness of photon capture and energy transduction. Addressing these issues is being facilitated by the development of patented novel "next-generation" high-throughput phenotyping platforms for higher plants (the Plant Phenometrics Array, PPA) and photosynthetic microorganisms (the Environmental Photobioreactor Array, ePBR). The PPA and ePBR technologies not only provide a powerful resource for use in PRL research, but also provide a major new resource for the scientific community studying photosynthesis and growth.

FY 2012 HIGHLIGHTS

A complete list of publications for the past year can be found at http://www.prl.msu.edu/publications. Research highlights include establishing key roles for thylakoid proton motive force in regulating the balance between photosynthetic efficiency and photoprotection (Kohzuma et al., 2012); discovering a novel regulatory pathway that controls the morphogenesis and proliferation of both peroxisomes and mitochondria (Aung & Hu, 2011); identifying a membrane-anchored GTPase that controls the structural integrity of the endoplasmic reticulum (Stefano et al., 2012); demonstrating that light-dependent regulation of cellular morphology in the cyanobacterium *Fremyella diplosiphon* is linked to cellular mechanisms that protect against photodamage and regulate photosynthetic efficiency and pigmentation (Singh & Montgomery, 2012); discovering a conserved mechanism by which cross-talk between the gibberellin and jasmonic acid (JA) hormone signaling pathways regulate the balance between growth and defense in flowering plants (Yang et al., 2012); demonstrating that a high turnover [FeFe]-hydrogenase maintains catalytic activity in micro-oxic cyanobacterial cells—herterosysts—in an aerobic milieu (Gärtner et al., 2012); and describing a signaling cascade by which the bacterial JA-mimicking toxin coronatine overcomes both stomatal- and mesophyll-based plant defenses (Zheng et al., 2012). In addition, to expand the scientific impact of the PPA and ePBR technologies, the PRL and Michigan State University have established the Center for Advanced Algal and Plant Phenotyping (CAAPP) to address decadal scientific challenges in the plant energy sciences.

Structure, Function, and Regulation of the Enzymes in the Starch Biosynthetic Pathway

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Students:	1 Postdoctoral Fellow(s), 2 Graduate(s), 2 Undergraduate(s)
Funding:	$70,000

A summary for this program was not available at press time.

Enzymology of Methanogenesis: Mechanism of Methyl-Coenzyme M Reductase

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Students:	2 Postdoctoral Fellow(s), 0 Graduate(s), 1 Undergraduate(s)
Funding:	$205,000

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% 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 H_2 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 H_2 and CO.

FY 2012 HIGHLIGHTS

By using substrate analogs and MCR variants, we have trapped reaction intermediates in the catalytic cycle and can rather definitively establish the mechanism of MCR. We also are determining how MCR is activated *in vivo*. We have discovered a CO-dependent cellular activation system and are determining the common cellular pathway for activation of MCR by H_2 and CO.

The Role of Phosphoinositides in Polarized Secretion of Cell Wall Components in Arabidopsis Root Hair Cells

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Students:	1 Postdoctoral Fellow(s), 1 Graduate(s), 1 Undergraduate(s)
Funding:	$180,000

PROGRAM SCOPE

The overall goal of this research proposal is to understand the molecular machinery that allows for the polarized targeting of cell wall components to the tips of growing root hair cells. In particular, we aim to understand how membrane trafficking compartments defined by presence of the plant regulatory GTPase, RabA4b, regulate this process and what role phosphoinositides (PI-4P) play during targeting of newly synthesized cell wall cargo to root hair tips in *A. thaliana*. To this end, we are using a combination of genetic, cell biological, and biochemical techniques. Our current working hypothesis is that RabA4b (along with other closely related RabA GTPase family members) is required for polarized secretion of cell wall components in root hair cells. The specific research aims of this project are to (1) investigate the molecular mechanisms by which RabA GTPases regulate proper targeting and delivery of secretory cargo to root hair tips; (2) examine whether cellulose synthesis occurs in the tips of root hairs, and if so, identify the molecular nature of these enzymes; and (3) determine the identity of four novel, temperature-sensitive root hair growth mutants, which we have termed loss of tip-localization (*ltl*) mutants.

FY 2012 HIGHLIGHTS

As of last year, we had uncovered a novel role for CSLD3, one member of a class of related CSLD cell wall synthases, during cell wall deposition in tip-growing root hair cells (published in *Nature Cell Biol., 13,* 973-80). In this last year, we have extended these investigations to examine the roles of other members of the CSLD family during cell wall synthesis in *A. thaliana*. Interestingly, we have shown essential functions of these proteins for the formation of phragmoplasts during cytokinesis. Specifically, we have discovered that expression of CSLD5, and a number of other cell wall biosynthesis genes, is controlled in a cell cycle-dependent fashion. This raises the intriguing possibility that a subset of cell wall synthetic genes may be specifically induced, and possibly required, for completion of cytokinesis in plants. Finally, we have identified and subsequently confirmed the mutated genes in two temperature-sensitive *ltl* mutants. While initially thought to be two independent mutants, both *ltl2-1* and *ltl2-2* mutants contain the same amino acid substitution in the extracellular lectin-like domain of a previously characterized receptor-like kinase, *FERONIA* (*FER*). Current experiments have focused on confirming the identity of this temperature-sensitive *FER* allele through complementation. Additionally, we have focused on attempting to identify the specificity of the FER lectin-like domain for various plant cell wall polysaccharides using in vitro carbohydrate binding assays.

Two-Dimensional Electronic Spectroscopies for Probing Electronic Structure and Charge Transfer: Applications to Photosystem II

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Sr. Investigator(s):	
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Funding:	$198,184

PROGRAM SCOPE

This research program focuses on key deficits in our current understanding of the PSII reaction center (PSII RC). Understanding the PSII RC's design principles has importance for both fundamental and applied sciences wishing to mimic its remarkable properties. The program aims to address the following open questions. (1) *What is the electronic structure of the PSII RC?* (2) *What is the charge transfer mechanism in the PSII RC?* (3) *What is the electronic structure and charge transfer mechanism in Acaryochloris marina?* (4) *Does electronic coherence facilitate energy transfer in the PSII RC?* To address these questions, we are utilizing two-dimensional electronic spectroscopy (2DES). We are also developing new variations on this method to more clearly separate the spectral signatures of energy transfer and charge separation.

FY 2012 HIGHLIGHTS

The past year has focused on continuing 2DES studies of the PSII RC using D1-D2-cytb559 complexes as a model system. We have published a "perspectives" article that describes the strengths of 2DES for studying natural light-harvesting systems and summarizes our recent work using 2DES to study the energy transfer and charge separation in the Qy band of the PSII RC [*Journal of Physical Chemistry Letters 2012*, 3, 503-510]. We were featured as the cover article and produced a video describing our PSII RC research. We have simulated 2DES spectra based on the most complete exciton model in the literature, showing that there are significant deviations between its predicted 2DES spectra and our data. This work was recently accepted for publication [*Journal of Physical Chemistry A* 2012, in press].

A significant part of the research program involves technique development for isolating charge separation processes. We have refined our 2DES with a continuum probe method, demonstrating that a chirped continuum can be used and spectral distortions can be readily corrected [*Selected Topics in Quantum Electronics, IEEE Journa*l of 2011, PP (99), 1-8]. We are currently applying this approach to enable probing of the Qy and ion bands to separate energy transfer and charge separation processes. We are also developing 2D electronic Stark spectroscopy that uses Stark shifts to isolate charge separation signatures. We have completed the construction of the experiment and will demonstrate the method on a charge transfer model system prior to studies of the PSII RC.

Functional Analysis of Plant Sucrose Transporters

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Funding:	$170,926

PROGRAM SCOPE

Plant sucrose uptake transporters (SUTs, also called SUCs) membrane proteins in the plasma membrane or vacuole membrane and are responsible for the H^+-coupled uptake of sucrose into the cytoplasm. These transporters are essential for the long-distance transport of sucrose in the phloem, vascular tissue in plants and for sucrose uptake into sink tissue such as seeds. The main goal of this project is to understand the structure/function relation of sucrose transporters. This will improve our ability to modify sucrose transporter activity and provide a mechanism to engineer changes in plant carbon partitioning in crop plants.

FY 2012 HIGHLIGHTS

We developed a new assay for sucrose transporter activity based on expression in yeast and fluorescent substrate uptake [Gora et al., Plant Methods 8:13 (2012)]. We used this assay in conjunction with gene shuffling and fluorescence activated cell sorting to study the structural basis for differences in substrate specificity between type I and type II sucrose transporters. We identified four amino acid changes that switch type II sucrose transporters to type I substrate specificity [Reinders et al., J Biol Chem 287 30296–30304 (2012)]. We used homology modeling to generate a 3D structure of OsSUT1 from rice. This allowed us to revise the transmembrane domain prediction for SUTs and to identify six conserved charged amino acid residues within transmembrane spans. Mutagenesis of these six positions revealed that five of the six are important for transport activity [Sun et al., Biochemistry 51: 3284-3291 (2012)].

Role of the Plant Cell Wall in Resistance to Pathogen Attack

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Funding:	$144,999

PROGRAM SCOPE

Plant cell walls are thought to present a physical barrier to attack by microbial pathogens. In addition to this structural effect, plants may sense changes in cell wall structure as indicators of pathogen attack. Yet, relatively little is known about the roles of plant cell walls in disease resistance. Previously, we have screened *Arabidopsis* thaliana mutants with altered cell walls for changes in disease resistance. Presently, we are working to understand how mutations impacting cell wall structure affect resistance. Specific goals are to (1) create multiply-mutant plant genotypes with more severe cell wall structure and disease phenotypes, (2) determine the nature of perturbations in the plant defense system responsible for altered disease phenotypes in cell wall mutants, and (3) test the hypothesis that Wall Associated Kinases (WAKs) link certain cell wall changes to activation of defense responses.

FY 2012 HIGHLIGHTS

We found that mutations in several different pectin methylesterase genes (PMEs) caused small but statistically significant increases in susceptibility to the bacterial pathogen *Pseudomonas syringae* pv. *maculicola* strain ES4326 (*Pma* ES4326). Plants with mutations in two or more PME genes allow approximately three-fold more bacterial growth than wild-type plants, indicating a positive role for PME genes in resistance. Using a gel-diffusion assay for PME activity, we have found that activity increases greatly in plants infected with *Pma* ES4326 or a necrotrophic fungal pathogen, *Alternaria brassicicola*. This increased activity does not occur in plants with defects in jasmonic acid signaling (*dde2*), a major sector of the plant defense signaling network. Defects in other major defense signaling sectors, including salicylic acid (*sid2*, *pad4*) and ethylene (*ein2*), do not affect PME activity. Using antibodies specific for methylesterified or demethylesterified pectin, we found that the degree of methylesterification declines over the course of infection by either *Pma* ES4326 or *A. brassicicola*.

Plant Recognition of CO/LCO Signals

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Funding:	$180,000

PROGRAM SCOPE

Synthesis of chitooligosaccharides (CO) is an ancient trait, found in organisms as diverse as bacteria and vertebrates. Substantial evidence implicates CO and chitin-like compounds in mediating cellular signaling events. For example, CO molecules induce plant innate immunity to invading fungal pathogens while, in legume plants, lipo-chitooligosaccharides (LCO) serve as key signals in the establishment of the nitrogen fixing symbiosis with soil bacteria. However, in addition to these better defined responses, both LCO and CO addition to plants has been reported to have wide ranging effects including stimulation of germination, increased photosynthetic efficiency, and plant growth. We believe that a substantial opportunity exists to contribute to our understanding of the signaling role of CO/LCO in eukaryotic development by studying their signaling response pathways in plants. Moreover, we believe that the findings from these studies will contribute to the overall understanding of how plants respond to environmental signals and integrate this information into overall physiology and development.

This work builds on our past identification of the key plant receptor for CO signaling, CERK1. The proposed work includes collaboration with Argonne National Laboratory to determine the x-ray crystal structure of LysM-domain proteins, similar to CERK1, define the quaternary structure of the CERK1 receptor complex, and elucidate elements of the downstream signaling cascade. An additional focus will be a second LysM-receptor like kinase, LYK4, which also appears to function in CO signaling. Finally, recent data suggest that smaller molecular weight CO, similar in size to the LCO nodulation signals, actually reduces innate immunity. We are investigating the mechanism by which this occurs using a variety of biochemical, genetic, and molecular approaches.

FY 2012 HIGHLIGHTS

Recent progress includes our publication that describes the important role that the LYK4 LysM-receptor-like kinase plays in CO signaling. Recent data indicate that LYK4 forms a complex with the CERK1 receptor. However, only CERK1 is essential for CO signaling with LYK4 playing an important, but non-essential, role. An additional member of the signaling complex was identified as a leucine-rich receptor-like kinase (termed PAMP-responsive receptor-like kinase 1, PRPK1). Biochemical studies have shown that PRPK1 is an active protein kinase. Work is continuing to determine the x-ray crystal structure of CERK1, LYK4, as well as other members of the receptor complex. A focus on the lab is to define the nature of CERK1-LYK4-PRPK1 interaction, as well as defining other members of this signaling complex. As noted below, we are also exploring the mechanism by which small molecular weight CO reduces the plant innate immunity response. We have shown that this inhibition occurs at the level of ligand-membrane interaction.

Novel Microbial Based Enzymatic CO_2 Fixation/Carboxylation Mechanisms

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Students:	0 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding:	$180,000

PROGRAM SCOPE

The research objective is to examine the catalytic mechanism of unique carboxylation enzymes involved in the metabolism of propylene and acetone. Studies of alkene and ketone metabolism have identified a central role for CO_2 and specifically CO_2 fixation reactions in these processes. The CO_2 fixing enzymes of the pathways are distinct carboxylases with unique molecular properties and cofactor requirements. We are utilizing a multidisciplinary approach involving kinetic studies, site specific amino acid substitution studies, and the determination of high resolution structures of enzymes in the presence of substrate, products, their analogs, and mechanism-based inhibitors to ascertain information concerning the biochemical mechanisms of enzyme catalyzed reactions.

FY 2012 HIGHLIGHTS

The most seminal accomplishment of the previous funding period was the structural characterization of 2-ketopropyl coenzyme M oxidoreductase/carboxylase (2-KPCC) with bound CO_2. Capturing target substrates or products can be difficult; capturing CO_2 at the active site of 2-KPCC has been a goal for some time but was extremely difficult. After screening numerous potential scenarios for capturing CO_2 at the active site, we found we were able to observe linear density consistent with CO_2 at the active site when crystals of 2-KPCC were soaked prior to data collection with the reaction products acetoacetate and CoM. Under these conditions, it appears that we were able to catalyze the back reaction and effective decarboxylation of acetoacetate to form CO_2 that remained bound at the active site. Serendipitously, the additional electron density in the active site could be fit to 2-ktopropyl coenzyme M (2-KPC), also consistent with the products of the back reaction, such that the position of CO_2 relative to 2-KPC indicates CO_2 is bound in a position ideal for electrophilic attack of the proposed carbanion intermediate. Additional accomplishments include defining the functional role of specific amino acid residues in catalysis for both 2-KPCC and the stereo selective R- and S- hydroxylpropylthioethane sulfonate dehydrogenases and defining a new class of FAD binding proteins in the structure of AbpE.

Role of HydF in Hydrogenase Maturation

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Students:	1 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding:	$185,000

PROGRAM SCOPE

The main goal of this project is to elucidate the biosynthetic steps for maturation of the [FeFe]-hydrogenase active site, the H-cluster, which contains biologically unusual ligands such as cyanide, carbon monoxide, and a nonprotein dithiolate. Two radical SAM enzymes (HydE and HydG) interact with the GTPase HydF to generate an H-cluster precursor that is transferred to the [FeFe]-hydrogenase to generate the active enzyme. Understanding the fundamental biochemistry and mechanistic steps by which these proteins produce a mature H-cluster and an active [FeFe]-hydrogenase is necessary to define the basic science underlying expression and activity of [FeFe]-hydrogenases. The fundamental insights we propose to obtain in this study therefore may subsequently be leveraged to rationally establish effective means to modulate the expression of active [FeFe]-hydrogenases for enhanced biological hydrogen production. The current project focuses on determining the stepwise sequence of events by which an H-cluster precursor is assembled on HydF, spectroscopic and structural characterization of iron-sulfur clusters on HydF, and elucidating the role of GTP binding/hydrolysis in H-cluster assembly.

FY 2012 HIGHLIGHTS

We have (1) shown that HydF can exist as either dimer or tetramer, and these two forms have different spectroscopic properties; (2) provided evidence that the dimeric state of HydF is more active in [FeFe]-hydrogenase activation than the tetrameric state; (3) used site-directed mutagenesis to probe the roles of highly conserved amino acids in HydF; (4) utilized CD spectroscopy to show that HydF can exist in two conformational states and that only one of these states is sensitive to GTP binding; and (5) utilized H/D exchange experiments to provide additional evidence for conformational changes in the presence of GTP.

P-type ATPases in Plants- Role of Lipid Flippases in Membrane Biogenesis

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

PROGRAM SCOPE

The long-term goals are to understand the structure and biological functions of P-type ATPases in plant cells. P-type ATPases include ion pumps that specifically transport H^+, Ca^{2+}, Zn^{2+}, Cu^{2+}, K^+, or Na^+, as well as an unusual subfamily (P4-type, or ALAs in Arabidopsis) that appear to flip lipids from one side of a membrane bilayer to the other. Flippases are proposed to (1) generate an asymmetric distribution of different lipids on each surface of specific membrane bilayers and (2) induce membrane curvature by forcing an unequal partitioning of phospholipids from one surface to the other. In plants, genetic evidence indicates that different subgroups have unique functions, some of which are essential to either reproductive development, tolerance to abiotic stresses such as hot days and cold nights, or normal growth and biomass accumulation. Research on lipid flippases and other P-type ATPase is expected to provide insights into energy conversion and storage. A better understanding of membrane biogenesis in plant cells has potential applications to engineering plants with new traits, including an increased production of lipids for biofuels.

FY 2012 HIGHLIGHTS

A double knockout of lipid flippases *ala6/7* was found to result in plants with a reduced seed set due to pollen tubes that grow slow and short. The concentrations of 144 different lipid molecular species were quantified for pollen grains from wild type and an *ala6/7* mutant. The mutant showed two significant changes—an increase in phosphatidic acid (PA) and a decrease in phosphatidylinositol (PI). The mutant was also found to have a more than 10-fold decrease in the amount of an FM-dye that can bind to the extracellular surface of the pollen tube plasma membrane. Our working model is that ALA6 and 7 flip PA from the exoplasmic surface of the cell to the interior. In the absence of this flipping, PA accumulates on the outside surface of the plasma membrane and thereby changes the charge density or membrane/matrix interactions that inhibit FM-dye insertion into the membrane surface. These results provide the first indication of a lipid flippase being involved in regulating the distribution and abundance of PA or PI—two membrane lipids with important roles in signaling and membrane structure.

Nanotube-Supported Phospholipid Bilayers

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Funding: $165,000

PROGRAM SCOPE

The overall long-term objectives of our BES DOE project are 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. In course of this project, we are (1) developing technology for fabricating homogeneous nanoporous substrates with desired pore dimensions and low light absorbance to enable biophysical studies of light-harvesting biomolecular systems, (2) investigating effects of surface chemistry through surface modification of nanoporous substrates on the lipid self-assembly and the properties of the lipid bilayers formed, and (3) developing and demonstrating lipid nanotube technology for building hybrid nanostructures based on membrane proteins. The main significance of our research program is in attaining fundamental understanding of the mechanism of lipid bilayer self-assembly under controlled conditions such as nanoscale confinement/imposed curvature, interfacial surface electrostatic and hydrogen-bonding interactions, as well as effects of membrane peptides and proteins on the mechanisms of self assembly. The ultimate outcome of our program is aimed at the development of experimental approaches for building robust functional hybrid nanostructures that could be used for biomimetic solar energy conversion and/or bioinspired separation technologies.

FY 2012 HIGHLIGHTS

We have developed a number of high throughput procedures for fabricating high quality nanoporous substrates with pore diameters ranging from 25 to 90 nm and exceptionally narrow (5 to 6 nm) pore diameter distributions. These substrates have been tested for incorporation of membrane proteins and subsequent structure-function studies of membrane proteins by solid state NMR. We have successfully labeled a photosynthetic reaction center (RC) from purple bacteria with a new electrostatic molecular tag we synthesized and characterized. A new pH-sensitive spin-labeled lipid was tested to assess surface electrostatics of lipid bilayer by EPR, and the results were compared with the Gouy-Chapman theory.

Pathogen Virulence Factors as Unique Probes of Plant Cell Structure and Function

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Funding:	$120,000

PROGRAM SCOPE

Our rationale is that by understanding how a collection of pathogen virulence factors act inside the host cell, we will better understand the normal, defense-relevant function of their targets. Our approach is a combination of structural biology, genetics, and plant-pathology. Our work, and similar work of others, has informed not only plant biology, but has provided important concepts in the understanding of mammalian innate immune function as well. This work fits the DOE remit to understand how the plant cell works as an energy producing factory. Of interest to this DOE program, our work combines experimental and computational tools from the physical sciences with biochemistry and molecular biology to achieve a more detailed understanding of the structure and dynamics of complex plant and non-medical microbial systems such as cell walls, biological motors, and cytoskeletal and other assemblies involved in energy capture, transduction, and storage. Ultimately, this research also addresses a problem that will vex biofuels production, namely pathogens usurping plant energy to their benefit and to the detriment of their plant hosts.

We focus currently on two families of type III effector proteins, HopAF1 and HopBA1, newly discovered through our ongoing medium throughput structural biology approaches. HopBA1 encodes a novel protein with structural homology to bacterial heme-binding proteins. HopBA1 triggers disease resistance in plants via a unique and novel TIR-X host innate immune receptor fragment. Further analysis of HopBA1 and its cellular targets will open new opportunities to understand the heretofore obscure cellular functions of the many innate immune receptor fragments encoded by plant genomes. HopAF1 has structural homology to bacterial toxin deamidases. We demonstrated a plausible and novel function for HopAF1 as an ethylene defense hormone-inhibiting enzyme that targets a key step in the Yang cycle, the biosynthetic pathway that uses methionine re-cycling to create ehylene. We propose to further verify this model and to understand the precise mechanism by which the broadly distributed HopAF1 proteins deamidate their targets.

FY 2012 HIGHLIGHTS

While we published nine peer-reviewed papers in very high profile journals, and despite four superlative reviews for our competitive renewal of this project, we were ultimately told that our project no longer fit the project remit and were given one year of funding to wind down the project. Karen Cherkis has defended her dissertation and successfully found a job in the local biotech industry. Erica Washington will defend this winter. Lead senior post-doc Marc Nishimura is looking for a faculty job. All’s well that ends well.

Sugar Sensing in Arabidopsis via AtRGS1

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Funding: $165,000

PROGRAM SCOPE

Understanding how plants sense sugars is critical for us to engineer crops that have greater energy yields. Our lab has shown that the signaling module called "G protein"-coupled signal transduction is a major means by which plants sense sugar and control the efficiencies of key plant physiologies such as photosynthesis and disease resistance, both of great interest to the DOE Bioenergy Science Program.

Transmethylation Reactions During Methylotrophic Methanogenesis in Methanogenic Archaea

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Funding: $165,000

PROGRAM SCOPE

Our DOE-sponsored project focuses on how methanogens produce methane from methylated compounds, such as monomethylamine (MMA), dimethylamine (DMA), or trimethylamine (TMA). We have described three distinct methyltransferases, one for each methylamine: MttB (for TMA), MtbB (for DMA), and MtmB (for MMA). Each methyltransferase methylates a cognate corrinoid protein. The TMA, DMA, and MMA corrinoid proteins are reduced to the active Co(I) form by the ATP-dependent iron-sulfur protein RamA. MtbA uses the methylated corrinoid proteins to methylate CoM, leading to methane formation. The sequence of the methylamine methyltransferase genes revealed that each of the non-homologous methyltransferases possess an in-frame amber codon that corresponds to pyrrolysine, the 22nd amino acid. As a result, the problem of understanding methanogenesis from methylated compounds now involves three questions: (1) *How is pyrrolysine made?* (2) *How is pyrrolysine genetically encoded by UAG codons in methylamine methyltransferase genes?* (3) *What function does pyrrolysine play in methylamine methyltransferases?*

FY 2012 HIGHLIGHTS

We have made progress in understanding an enzyme key to the insertion of pyrrolysine into methylamine methyltransferases: the pyrrolysyl-tRNA synthetase (PylS). We have identified a unique tRNA binding domain which allows PylS recognition of the pyrrolysine-tRNA. We have also identified residues in the amino acid binding pocket of PylS necessary to recognize pyrrolysine at low concentrations for insertion into the methylamine methyltransferases. We have further built on our

DOE-funded 2011 Nature paper that described the pathway of pyrrolysine biosynthesis, and employed deuterium labeling to illustrate a probable mechanism of how lysine is converted into the ring of pyrrolysine. We continued our site-directed mutagenesis experiments to test the interaction of pyrrolysine and surrounding residues in the active site. We have just completed two vectors that will allow us to eliminate the two copies of the MMA methyltransferase gene in a host organism, thereby providing a background-free host in which to express MMA methyltransferase genes with desired mutations. Additionally, we have examined a highly similar homolog of the TMA methyltransferase lacking pyrrolysine; and we established this is not TMA methyltransferase, but is instead a novel glycine betaine methyltransferase. We are also preparing mutants of the TMA methyltransferase lacking pyrrolysine for synthesis in a host recombinant methanogen system in order to explore the role of pyrrolysine in the dissimilar MMA and TMA methyltransferases, which lack all sequence similarity but for pyrrolysine. In the coming period, we will use these mutations in order to focus entirely on the biochemical role of pyrrolysine and to discover why this unique residue is necessary for methylamine-dependent methyl transfer under anaerobic methanogenic conditions.

The Structure of Pectins

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Funding:	$122,091

PROGRAM SCOPE

The goals of this project are threefold. The first is to gain a complete picture of the organization of the various regions within pectin molecules; the second is to characterize the linkage between pectins and xyloglucan; and the third is to identify transglycosylases out in the cell wall that attach the different cell wall polymers to each other to make the final crosslinked structure.

The approach to the first two objectives is to used cloned mono-specific enzymes to selectively take apart cell walls so that we can purify informative fragments and determine their structures by NMR and mass spectrometry. For the third objective, we plan to use beads carrying hydrazides to which we can covalently link oligosaccharides. After incubation of the derivatized beads with potential polysaccharide donors and plant extracts, followed by extensive washing, we will look for new additions to the beads by digesting with enzymes which work on the potential donor and analyzing the solubilized products by capillary electrophoresis.

FY 2012 HIGHLIGHTS

We have isolated a mixture of two or three closely related oligosaccharides that contain both a xylogalacturonan (XGA) segment and an rhamnogalacturonan (RG) segment. The linear structure of the individual oligomers was determined by electrospray MS/MS, and the nature of the linkages between the sugars was inferred from NMR spectroscopy of the mixture. We can conclude that RG is linked to the non-reducing terminus of XGA.

Other oligosaccharides we have isolated indicate that homogalacturonan is linked to the non-reducing terminus of RG.

Protein Complexes Involved in Syntrophic Hydrogen Production and Electron Transfer

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Funding:	$194,220

PROGRAM SCOPE

Syntrophic metabolism is an essential component of the global carbon cycle and is critical to efficient waste treatment and biofuel production. Syntrophy is a thermodynamically necessary interaction where the activity of two organisms is needed to metabolize the growth substrate. One organism keeps hydrogen and formate levels low, which allows the second organism to make hydrogen or formate from its growth substrate. The production of hydrogen or formate from electrons generated in the oxidation of fatty and aromatic acids requires energy even at low hydrogen and formate concentrations. Energy used to drive these unfavorable redox reactions is believed to come from ion gradients. Thus, the membrane components involved in the generation and use of ion gradients are critical components of syntrophic metabolism. The objectives of this proposal are to (1) detect the membrane complexes involved in electron transfer and hydrogen production; (2) identify gene systems induced under syntrophic growth conditions; (3) determine the functions of a butyrate-induced, membrane complex in *Syntrophomonas wolfei* and an NADH:ferricyanide oxidoreductase activity in *Syntrophus aciditrophicus*; and (4) determine whether *S. wolfei* and *S. aciditrophicus* have electron-bifurcating hydrogenases and formate dehydrogenases. We will use a combination of proteomic and transcriptomic approaches to detect complexes involved in electron transfer and hydrogen production during syntrophic fatty and aromatic acid metabolism. Complexes of interest will be further characterized to determine the subunit composition, presence of cofactors, and activity.

FY 2012 HIGHLIGHTS

We developed a new method to grow large volumes (200 liters) of syntrophic cocultures. We now have sufficient biomass (365 g of the *Syntrophomonas wolfei* and *Methanospirillum hungatei* coculture) for our biochemical studies. We discovered a membrane complex in *S. wolfei* that is highly up-regulated during syntrophic butyrate growth. We surveyed the membrane complexes in *S. aciditrophicus* using blue-native gel electrophoresis and liquid chromatography-tandem mass spectroscopy and found several ion-translocating complexes including ATP synthase, pyrophosphatase and glutaconyl-coenzyme A decarboxylase.

Genes Needed for H_2 Production by Sulfate Reducing Bacteria

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PROGRAM SCOPE

Syntrophy involves an obligate interaction between two species and occurs during the degradation of certain organic compounds such as fatty and aromatic acids. Using a screen for growth with a Syntrophic bacterium, mutants in *Desulfovibrio alaskensis* were identified in genes required for syntrophy. Several genes were identified that are needed for syntrophic growth. This included two groups of interesting mutants: genes involved in respiration as well as genes for cellular structures, specifically flagella and cell wall, membrane and extracellular polymer synthesis. One of the mutants is in the RNF complex, a membrane-associated respiratory complex known to be involved in harnessing an ion gradient to generate reduced ferredoxin. The RNF mutants obtained here do not grow with H_2, suggesting that RNF in *Desulfovibrio* obtains electrons from H_2. Virtually all of the non-respiratory mutants are deficient in biofilm formation and many are non-motile. RNA expression experiments have shown large increases in the above groups of biofilm/motility-related genes, implicating the formation of biofilm/cell aggregates in Syntrophic interaction. Flagellum structural genes and flagellum biosynthesis genes are also highly upregulated during syntrophic growth. Their role could be either in location of the Syntrophic partner or in stabilization of the syntrophic aggregate as flagella are observed microscopically to link cells in aggregates. The one gene that is most highly induced during syntrophic growth in *Desulfovibrio* is the alcohol dehydrogenase, known to be needed for growth on ethanol. These results suggest a role for alcohols in the Syntrophic interaction. These processes will be further studied.

FY 2012 HIGHLIGHTS

We have obtained expression data comparing Syntrophic growth to pure culture growth for both *Desulfovibrio alaskensis and Syntrophomonas wolfei*. This data is currently being analyzed. We have also developed a Chemotaxis assay that will be used to study motility towards the syntroph and chemicals.

Molecular Mechanisms of Plant Cell Wall Loosening

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Funding: $170,000

PROGRAM SCOPE

We are studying the biophysical and molecular bases of plant cell wall loosening, which is essential for cell growth and is connected to other developmental processes, to plant defense, and to new technologies for engineering plant growth and for bioconversion of cell walls into useful materials and biofuels. 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 resistance to physical treatments.

FY 2012 HIGHLIGHTS

We used site-directed mutagenesis, in combination with a crystal structure of the bacterial expansin BsEXLX1, to identify the amino acid residues essential for wall-loosening activity and for binding to cell walls and to cellulose. We discovered that the protein binds to cell walls by two distinct mechanisms using different surfaces of the protein. Binding to pectins is electrostatic in nature and depends on nonconserved basic amino acids on the surface of the D2 domain. This type of binding can be reduced by site-directed mutagenesis and wall creep activity of the protein increases—indicating it is not essential for expansin activity. In contrast, binding to cellulose is mediated by three aromatic residues arranged linearly on the D2 surface. Wall loosening activity requires cellulose binding by domain D2 but additionally requires specific residues on the surface of domain D1. We further characterized the binding of expansin to cellulose by a combination of binding isotherms, isothermal titration calorimetry, and x-ray crystallography. The results indicate that expansin binding to the cell wall is entropy driven and depends primarily on a linear set of hydrophobic residues on the protein surface—much like type-A cellulose binding domains. Further, we produced crystals of a complex of BsEXLX1 with cellohexaose and obtained a molecular structure (1.95 Angstrom) which displayed a unique feature: the ligand is sandwiched between the strip of aromatic residues in the two EXLX1 proteins. The results support the idea that D2 binds to cellulose via a hydrophobic interaction largely driven by entropy, i.e., disrupting the organized water layer at the surface of cellulose and the expansin binding surface.

New Perspectives on Acetate and One-Carbon Metabolism in the Methanoarchaea: Carbonic Anhydrase

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Funding: $150,000

PROGRAM SCOPE

Prokaryotes encode three independently evolved classes (α, β, and γ). Although wide-spread in prokaryotes, only three γ-class enzymes have 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 CA. 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 CAs 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 2012 HIGHLIGHTS

The γ-class CA from anaerobe *Pelobacter carbinolicus* (domain *Bacteria*) was biochemically characterized. The enzyme produced in *Escherichia coli*, and purified anaerobically, contained an iron:zinc ratio of 23:1. The effective k_{cat} (normalized to metal content) was $13.2 \pm 5.2 \times 10^{-4}\ \mathrm{s}^{-1}$. The enzyme lost all activity when exposed to air, a result consistent with oxidation of ferrous iron to ferric that is lost from the active site. The results suggest iron is the preferred metal for catalysis by the gamma CA from *P. carbinolicus*.

The active site residues of Cam have no resemblance to any CA for which the catalytic mechanism is known except for two residues (Trp19 and Tyr200) positioned similar to Trp5 and Tyr7 important for catalysis in the human alpha class HCA II. Trp19 and Tyr200 were investigated by structural and kinetic analyses of replacement variants. Steady-state k_{cat}/K_m and k_{cat} values decreased 3- to 10-fold for the Trp19 variants whereas the Y200 variants showed a 5-fold increase in k_{cat}. Rate constants for proton transfer decreased nearly 10-fold for the Trp19 variants, and an increase of ~2-fold for Y200F. The pK_a values for the proton donor decreased ~2-fold for Trp19 and Y200 variants. The variant structures revealed a loop composed of residues 62-64 that occupies a different conformation than previously reported. The results show that, although Trp19 and Y200 are non-essential, they contribute to an extended active-site structure distant from the catalytic metal that fine tunes catalysis. Trp19 is important for both CO_2/bicarbonate interconversion, and the proton transfer step of catalysis. The results extend an understanding of the active site and catalytic mechanism of Cam which further contributes to a general understanding of the gamma class.

Functional Analysis and Genetic Manipulation of Plant ABCB Organic Ion Transporters

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

PROGRAM SCOPE

In yeasts and plants, a large and diverse family of ATP-binding cassette (ABC) transporters mediate the movement of metabolites, cell wall monomers, secondary compounds involved in plant protection and signalling, 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 2012 HIGHLIGHTS

(1) Characterization of the reversible transport mechanism of the Arabidopsis ABCB4 transporter. Results generated in this study demonstrate that ABCB4 is a substrate-activated transporter; suggest that 2,4-D is a non-competitive inhibitor of IAA transport by ABCB4; and demonstrate that ABCB4 is an ideal model for studies of ABCB transporter reversibility. Published in *The Plant Journal.*

(2) Demonstration that uptake mediated by ABCB4 in Arabidopsis roots is distinct from uptake mediated by the LAX1 and LAX2 permeases. In collaboration with Dr. Ranjan Swarup (University of Nottingham), LAX proteins were distinguished from ABCB activity. Published in *The Plant Cell.*

(3) Dependence of Arabidopsis ABCB19 trafficking and membrane stability on long chain fatty acids, sphingolipids, and structural sterols. The model ABC exporter used in this project (ABCB19) exhibits a very high degree of substrate specificity and recruits a proton ATPase, ABCB1, and PIN1 to sphingolipid and sterol-enriched membrane domains to motivate long-distance transport of the compound indole-3 acetic acid from the shoot to root apex. Mutants and pharmacological inhibitors were used to show that structural sterols and sphingolipids are required for ABCB19 activity. The TWD1/FKBP42 co-chaperone immunophilin was shown to be required for exit of ABCB19 from the ER, but ABCB19 interactions with sterols, sphingolipids, and PIN1 were shown to be spatially distinct from FKBP42 activity at the ER. Modelling and activity assays demonstrate the feasibility of mutational analyses with this model transporter. Published in *The Plant Journal.*

Regulation of Carbon Allocation to Phenylpropanoid Metabolism

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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.

FY 2012 HIGHLIGHTS

We have found that the phenotype of a lignin-deficient Arabidopsis 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, and suggests that targeting of the transcription machinery, or the signal transduction machinery that relays information on perturbations in phenylpropanoid metabolism to it, may be viable strategies to improve bioenergy crops.

Conformational and Chemical Dynamics of Single Proteins in Solution by Suppression of Brownian Motion

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Funding:	$229,749

PROGRAM SCOPE

The objective of our program is to perform detailed examinations of the solution-phase conformational and photodynamics of single biomolecules critical to photosynthesis, in particular, light harvesting antenna proteins and redox electron-transfer enzymes. To study a single biomolecule in solution, we utilize our recently developed ABEL trap (Anti-Brownian ELectrokinetic trap), which cancels out a single protein's Brownian motion in solution, and thus provides a means to greatly extend the time available for making single-molecule measurements by a factor of 1000x *without* resorting to the binding of the protein to a surface or the confinement of it in a transparent host medium, both of which can significantly alter the "true" properties of the molecule. We measure multiple parameters for each molecule, such as brightness and excited state lifetime, and use detailed biophysical modeling to extract potential mechanisms for the observed photodynamics. These processes should enable a deeper understanding of the lifecycle of antenna proteins, and of the exact mechanism of the electron transfer redox process in metalloenzymes.

FY 2012 HIGHLIGHTS

We have had particular success in employing the ABEL trap to explore conformational and photo-dynamics of single allophycocyanin antenna proteins via simultaneous intensity and lifetime measurements, and have now extended these studies to the bacterial light-harvesting protein LH2 and to the wavelength dependent photodynamics of single monomers of allophycocyanin. In addition, we have published our first study of the detailed kinetic behavior of a redox enzyme in the ABEL trap, nitrite reductase, which catalyzes the one-electron reduction of nitrite to NO. This work was enabled by single jumps in the brightness of a reporter dye attached to the enzyme which represent the transfer of a single electron from a Type I Cu to a Type 2 Cu site. By adding the ability to sense spectral changes for the molecule in the trap, we observed unexpected spectral shifts in the emission of single molecules of peridinin-chlorophyll-protein, and have used simultaneous lifetime/brightness/spectral measurements of allophycocyanin monomers to determine the exact sequence of photo-induced changes in the pigment molecules in the antenna. In the methods development arena, we have extended the abilities of the ABEL trap by a novel high-speed beam scanning pattern, and by analysis of the innovation errors in the Kalman filter controlling the feedback, we can extract real-time estimates of the diffusion coefficient and the mobility of the single molecule in the trap. These developments have allowed us to trap a single small oligonucleotide consisting of only 30 T bases labeled by only one fluorophore, and trapping of a single small emitting molecule is on the horizon.

Mechanism and Function of the Chaperonin from Methanococcus Maripaludis: Implications for Archaeal Protein Homeostasis and Energy Production

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Funding:	$170,000

PROGRAM SCOPE

Methanococcus maripaludis is an archaeal organism of great relevance to understanding the biological production of energy and eventually harnessing such knowledge for biofuel production. As a methanogen, *M. maripaludis* obtains energy by sequestering H_2 and reducing CO_2 to methane by the methanogenic pathway. Thus, understanding how this organism assembles macromolecular protein complexes and how it maintains and regulates their function could have important practical implications, in addition to being a fundamental scientific question. Similar to other archaea, very little is know about the mechanisms and pathways that promote protein folding and maintain protein homeostasis in *M. maripaludis*. This proposal is focused on understanding the central player of its protein folding machinery, namely the group II chaperonin complex Mm-Cpn. Through a combination of biochemistry, systems biology, biophysics, and structural biology, our work will (1) identify the archaeal substrate repertoire of Mm-Cpn and (2) define mechanistic and structural principles of Mm-Cpn mediated protein folding. 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.

FY 2012 HIGHLIGHTS

This grant started on September 1st 2012. In this very short time, we have recruited two very talented researchers: a graduate student that will carry out the *in vivo* analysis of substrates and a post-doc that will spearhead the biophysical characterization. We have designed a number of specific tags in internal loops for labeling and purification, and will begin *in vivo* expression and SILAC labeling in the new year.

Ferredoxin-Dependent Plant Metabolic Pathways

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

PROGRAM SCOPE

The iron-sulfur protein ferredoxin, located in the cytoplasm of cyanobacteria and in the soluble stromal space of chloroplasts in photosynthetic eukaryotes, is reduced by Photosystem I in a light-dependent process; and the reduced protein subsequently serves as the physiological donor for many enzymes that play key roles in carbon, nitrogen, and sulfur metabolism in oxygen-evolving photosynthetic organisms. Reduced ferredoxins, which are low-potential, one-electron carriers, also serve 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 phytobilins. The goal of the project is to elucidate the mechanisms of the multi-electron reaction enzymes that use reduced ferredoxin as the electron donor and to elucidate the details of the interactions of ferredoxin with these enzymes by using structural techniques and site-directed mutagenesis to identify the protein/protein interaction domains involved in the formation of ferredoxin/enzyme complexes.

FY 2012 HIGHLIGHTS

The roles of four absolutely conserved in the ferredoxin-dependent nitrate reductase from the cyanobacterium *Synechococcus* sp. PCC 7942 have been investigated. Replacement of either Lys58 or Arg70 by glutamine results in a complete loss of activity, with either reduced ferredoxin or a non-physiological electron donor. K58R and R70K variants are also inactive, indicating a specific requirement for these two amino acids, rather than simply having a requirement for a positive charge. Replacement of Lys130 by glutamine causes substantial, but not total loss of activity, while replacement by arginine at this position has less effect. Replacement of Arg146 has no significant effect on activity. Replacement of Lys58 causes large losses of both the Mo-pterin and iron-sulfur cluster prosthetic groups and makes the cluster much more susceptible to oxidative damage. With the exception of the large decrease in the affinity of ferredoxin binding exhibited by the K58Q variant, these mutagenic replacements have relatively small effects on substrate-binding affinities. An *in silico* three-dimensional model of the enzyme has been used to provide a rationalization for these results.

Cyanobacteria accomplish arsenate detoxification by an initial 2-electron reduction of arsenate, followed by an ATP-dependent removal of arsenite. The arsenate reductase from *Synechocystis* sp. PCC 6803 uses one of its three glutaredoxins, glutaredoxin A, as its preferred electron donor. A structure of glutaredoxin A, at 1.8 Å resolution, has been obtained. Site-directed mutagenesis was used to demonstrate that only one of the two cysteines at the active site of glutaredoxin A, Cys15, is required for its activity as an electron donor to arsenate reductase. Site-directed mutagenesis was also used to demonstrate that only three of the five cysteine residues present in the reductase (Cys8, Cys80, and Cys82) are essential for activity, while the other two (Cys13 and Cys35) are not. Results from these mutagenic studies have been combined with *in silico* structural modelling and kinetic studies to provide support for a proposed mechanism and to identify a key enzyme intermediate.

Using the Corngrass1 Gene to Enhance the Biofuel Properties of Crop Plants

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Funding:	$153,496

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 2012 HIGHLIGHTS

We transformed switchgrass with five different promoters driving the *Cg1* gene in aerial tissue and not in roots. The promoters were chosen due to their putative green tissue specific expression patterns. All promoters gave the expected phenotype of increased branching, but some were more severe than others. A senescence induced promoter worked well in increasing branching without reducing overall biomass. The plants have been transferred to the field to obtain data on cell walls and biomass. We also transformed the *Cg1* gene into sorghum and wheat in a collaboration with Tom Clemente at the University of Nebraska. These plants are fixed in the juvenile phase of development and also have increased axillary branching.

We made progress in obtaining knock-outs of the *SPL* genes, which are targeted by the *Cg1* microRNA. Plants that carry insertions in both *SPL5* and *SPL7* genes have increased branching and narrow leaves. This result suggests that it is loss of these specific *SPL* genes that produce the branching phenotypes seen in *Cg1* overexpressors.

Jasmonate Hormone: Regulating Synthesis of Reduced Carbon Compounds in Plants

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Funding:	$200,000

PROGRAM SCOPE

Our original interest in understanding the role of JA in regulating the final stages of stamen and pollen development led to our discovery of the JAZ repressors, and the molecular mechanism of jasmonate (JA) hormone 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, and (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 2012 HIGHLIGHTS

Our ongoing research on this project aims to identify the transcription factor(s) that is inhibited by JAZ and mediates MYB21 expression in stamens in response to jasmonate. We conclude that MYC3 (At5g46760) and MYC4 (At4g17880) are JAZ-interacting transcription factors that act together with MYC2 to activate jasmonate responsive genes, including the JAZ genes. In our yeast-two-hybrid and pulldown assays, MYC5 interacted poorly with JAZ proteins. However, plants overexpressing MYC5 exhibited enhanced and constitutive jasmonate responses similar to plants overexpressing MYC3 or MYC4.

The lack of jasmonate phenotypes in myc3 and myc4 mutants suggested that redundancy may exist among the JAZ-regulated transcription factors. One strategy to possibly overcome such redundancy is to express a cDNA that accomplishes the addition of an EAR motif (e.g., LDLDLELRLGFA) to the target transcription factor. This can convert transcriptional activators to repressors by recruiting the TOPLESS corepressor to the transcription complex. We produced transgenic plants expressing MYC2-EAR, MYC3-EAR, MYC4-EAR, and MYC5-EAR constructs. The MYC2-EAR plants exhibit a myc2 mutant phenotype, while plants expressing MYC3-EAR or MYC4-EAR were not distinguishable from wild-type. However, several lines expressing MYC5-EAR were partially or completely male-sterile. We are performing experimental tests to examine whether or not expression of the MYC5-EAR protein is responsible for the male-sterile phenotype, and whether or not the effect is through blocking jasmonate responses. These include cosegregation analysis, pollen germination assays, and experiments to test whether MYC5-EAR plants are blocked in other jasmonate responses.

Lignin Biopolymer Assembly and Primary Structure: A (Bio)Chemical Characterization

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Funding:	$160,000

PROGRAM SCOPE

Lignins, the second most abundant biopolymers in vascular plants, are of considerable importance in considering both renewable energy strategies from biomass, and their use as, e.g., petrochemical substitutes for polymer applications. Lignins are also largely responsible for so-called lignocellulosic recalcitrance. Yet, vascular plant evolution appears to have largely hinged on the capability to produce lignins. They help reinforce plant cell walls in the vasculature, thereby enabling vascular plants to stand upright to dynamically respond to different environmental effects, and in providing conduits for water/nutrient transport *in planta*. Early considerations suggested lignins were 3D cross-linked polymers, randomly assembled, and similar to thermosets. However, various analyses established they are more linear (thermoplastic like). There is much need to develop new means to identify lignin polymer primary structure, as well as to better understand effects of reduction in lignin levels, or their compositional modifications, in plant tissues. However, the latter needs to be done without deleteriously affecting plant growth and development, or adversely affecting tissue biophysical/biomechanical properties.

FY 2012 HIGHLIGHTS

The first highlight describes arogenate dehydratase (ADT) *Arabidopsis* mutants having vastly different levels of lignin, encompassing a range spanning from near wild type levels to reductions of up to ~68% (Corea et al, JBC, 2012).

A second highlight assessed a putative proton relay in *Arabidopsis* cinnamyl alcohol dehydrogenase catalysis (Lee et al, Organic Biomolecular Chemistry, in press). Following our structural biology investigation of AtCAD5, roles of three amino acid residues in a putative proton relay system (Thr49, His52, and Asp57) were investigated.

A third highlight studied the ternary complex, catalytic mechanism, and substrate versatilities of hydroxycinnamoyl CoA:shikimate hydroxycinnamoyl transferase (HCT) and hydroxycinnamoyl CoA:quinate hydroxycinnamoyl transferase (HQT). The overall catalytic mechanism including an x-ray crystal structure analysis (of the apo-form, binary and ternary complexes with *p*-coumaroyl CoA and shikimic acid) was completed.

The Rhizobial Nitrogen Stress Response and Effective Symbiotic Nitrogen Fixation

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Funding:	$170,000

PROGRAM SCOPE

The supply of usable nitrogen compounds like ammonia or nitrate often limits plant growth. In contrast with most plants, legumes like alfalfa and soybean can associate with bacteria called rhizobia to obtain their needed nitrogen via this symbiotic relationship. The legumes fix carbon by photosynthesis and provide carbon compounds to the rhizobia, which then use energy and reductant generated by degrading these carbon compounds to reduce atmospheric dinitrogen. Better understanding of metabolism and regulation in these symbioses is likely to be crucial to increasing their production of ammonia. There are three reasons that DOE is interested in this process: (1) the alternative way of generating usable nitrogen uses about 5% of the world's natural gas, (2) 1 kg of nitrogen can support the generation of about 50 kg of biomass, and (3) without industrial nitrogen fixation, agriculture could support only about 40% of the world's current population.

With our DOE grant support, we are studying a unique mutant of *Sinorhizobium meliloti* Rm1021 that fixes nitrogen in symbiosis with alfalfa at a normal rate, but the symbiosis is not "effective"—the alfalfa does not grow well without a nitrogen supplement. The mutation is in *glnD*, the gene that encodes a major bacterial N sensor. The mutant GlnD signals that N is abundant even when it is not. We have shown that the mutant bacteria export fixed N to the plant and that the unusual Fix+Eff$^-$ phenotype persists even when other regulatory components of the nitrogen stress response (NSR) are removed. We have proposed that the regulatory defect in GlnD interferes with a mechanism used to coordinate symbiotic metabolism and results in the bacteroids diverting the fixed N into an N-containing compound that the plant cannot metabolize.

FY 2012 HIGHLIGHTS

The experiments carried out during 2012 are directed at understanding how the *glnD* mutation causes the unusual phenotype and what this phenotype means at a metabolic level. We have analyzed free-living gene expression in Rm1021 and various isogenic derivatives with mutations in NSR regulatory genes and have found a subclass of genes that are controlled by GlnD but not by the other regulatory genes in the NSR. The analysis shows that some of the regulatory genes that have been assigned to the NSR may have other functions in the cell. In collaboration with scientists at Pacific Northwest National Laboratory, we have examined very deep proteomes of *S. meliloti* in symbiosis and free-living culture and found interesting differences between them. Our data also show that the tissues associated with the mutant bacteria contain new metabolites predicted to contain nitrogen. We are attempting to determine the identity of these using mass spectroscopy and NMR.

Unraveling the Regulation of Terpenoid Oil and Oleoresin Biosynthesis for the Development of Biocrude Feedstocks

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Funding:	$340,000

PROGRAM SCOPE

Terpenoid oils and oleoresins are characterized by a high volumetric energy density and high degree of reduction, and are thus viable biocrude feedstocks for liquid transportation fuels comparable to diesel and kerosene. A long-term goal of my laboratory is to develop quantitative conceptual models of terpenoid oil/oleoresin biosynthesis in plants that can guide researchers in developing superior terpenoid biofuel/biomaterial feedstocks. However, because these pathways are confined to specialized epithelial gland cells, which are scarce and not readily accessible to experimentation, pathway regulation is thus far poorly understood. We have made considerable advances in developing protocols for the isolation and biochemical characterization of metabolism in various types of epithelial gland cells, progress that has put us in a unique position to experimentally address gaps in our understanding of the regulation of terpenoid oil and oleoresin biosynthesis. We are currently using three experimental model systems to evaluate terpenoid pathway regulation: (1) peppermint essential oil glandular trichomes, (2) *Citrus* peel essential oil cavities, and (3) pine resin ducts. The proposed activities are designed to address critical gaps in our knowledge of how plants store energy in the form of terpenoid oils and oleoresins.

FY 2012 HIGHLIGHTS

We developed a second-generation kinetic mathematical model of peppermint oil gland monoterpene biosynthesis. We are now able to accurately describe biochemical, developmental, environmental and genotypic determinants of essential oil composition and yield. [Rios-Estepa R., Lange I., Lee J.M.**,** Lange B.M. (2010) Mathematical modeling-guided evaluation of biochemical, developmental, environmental and genotypic determinants of essential oil composition and yield in peppermint leaves. *Plant Physiol.* 152, 2105-2119 (COVER STORY). Lange B.M., Rios-Estepa R. (2012) Kinetic modeling of plant metabolism and its predictive power – peppermint essential oil biosynthesis as an example. *Methods Mol. Biol.*, in press.]

Building on our mathematical modeling data, we developed metabolic engineering approaches, which led to the successful generation of various transgenic peppermint lines with favorable oil composition and dramatically increased oil yields. [Lange B.M., Mahmoud S.S., Wildung M.R., Turner G.W., Davis E.M., Lange I., Baker R.C., Boydston R.A., Croteau R.B. (2011) Improving peppermint essential oil yield and composition by metabolic engineering. *Proc. Natl. Acad. Sci. USA* 108, 16944-16949.]

We determined the regulatory characteristics of the monoterpene biosynthetic pathway at the transcriptional, posttranslational and metabolite accumulation level and were able to correlate these data sets with microscopic measurements of oil cavity volumes. As part of this effort, we obtained cell type-specific transcriptome data from isolated *Citrus* peel epithelial cells lining secretory cavities and evaluated the biosynthetic capabilities of these specialized cells. [Voo S.S., Turner G.W., Grimes. H.D.,

Lange B.M. (2012) Assessing the biosynthetic capabilities of secretory glands in *Citrus* peel. *Plant Physiol.* 159, 81-94.]

Biohydrogen Production by a Photosynthetic Bacterium

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Funding:	$170,000

PROGRAM SCOPE

Our overall goal is to generate foundational knowledge that will improve our ability to use dense suspensions of photosynthetic bacteria as biocatalysts to convert inexpensive feedstock compounds to hydrogen gas or other biofuels. Towards this end, we are unraveling signal transduction cascades involved in the regulation of photosynthesis at low light.

The anoxygenic photosynthetic bacterium *R. palustris* generates energy from light by cyclic photophosphorylation under anaerobic growth conditions. Unlike many related bacteria, it can respond to low light intensity to more efficiently harvest light. Previous work showed that expression of *pucBAd*, the operon encoding the low light LH4 antenna complex, is controlled by a bacteriophytochrome (BphP)-initiated signal transduction system. The details of how this signaling system operates have not yet been worked out, but it involves phosphotransfer reactions that we thought were initiated by light absorption. Two BphPs, designated BphP2 and BphP3, are configured as light-regulated histidine kinases that control expression of the operon encoding the LH4 antenna complex. Structural and biophysical studies have shown that BphP2 and BphP3 respond to light quality by reversible conversion between a red absorbing form and a far red or a near red absorbing form for BphP2 and BphP3, respectively. Photoconversion requires incorporation of the light-absorbing chromophore biliverdin into the protein. We initiated studies to investigate how *R. palustris* might sense light intensity as a function of light quality via its bacteriophytochromes.

FY 2012 HIGHLIGHTS

(1) We determined that BphP2 and BphP3 are both required for the expression of the low light LH4 antenna complex under anaerobic conditions. However, since biliverdin requires oxygen for its synthesis by heme oxygenase, it was unclear to us how BphPs in anoxygenic bacteria are able to function.

(2) We showed that BphP2 purified from anaerobically-grown cells has a small amount of bound biliverdin. We also determined that biliverdin requires one particular *R. palustris* heme oxygenase for its synthesis. This heme oxygenase likely has a high affinity for oxygen, which allows it to synthesize some biliverdin even under apparently anoxic conditions.

(3) We were surprised to find that deletion of the *R. palustris* heme oxygenase or mutations in the BphPs that prevent biliverdin binding did not disrupt BphP activity under anaerobic conditions. This indicates that BphP2 and BphP3 do not require biliverdin to function under anaerobic conditions and the apophytochrome form of the BphP is sufficient for its activity. Instead, the main driver of LH4 gene expression under these conditions was light intensity, not light quality.

(4) The bacteriophytochrome with is chromophore does subtly fine tune expression of the LH4 system in response to changes in light quality.

Computational Design of Proteins, Molecules and Materials with Novel Chemistrie

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Funding:	$150,000

PROGRAM SCOPE

Computational design of hybrid protein-organometallic molecules and materials, combining the specificity, affinity, and modularity of proteins with the potent chemical reactivities of molecular catalysts. We apply our methodology to the design of a wide range of peptides, proteins, and small molecules, as well as interfaces between these components.

FY 2012 HIGHLIGHTS

The widely used Rosetta and RosettaDesign software has been extended to model novel protein/small molecule catalysts in which one or many small molecule active centers are supported and coordinated by protein scaffolding. Symmetric modeling and design of scaffolding has been developed and applied. Peptide sequences for organometallic coordination and material assembly have been designed, synthesized, and characterized experimentally. Symmetrical outer coordination scaffolds for the DuBois nickel phosphine hydrogenase have been designed, and techniques for synthesis and characterization of these constructs are in development with collaborators DuBois and Shaw.

Electron Flow and Energy Conservation in a Hydrogenotrophic Methanogen

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Funding:	$180,000

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 2012 HIGHLIGHTS

Mutants of *Methanococcus maripaludis* lacking hydrogenases proved useful in demonstrating the role of Eha. In one mutant, six hydrogenases were missing, leaving Eha as the only hydrogenase. This mutant required both formate and hydrogen for methanogenesis and growth, and since the hydrogen was required in low amounts, the function of Eha could only be anaplerotic. In addition, hydrogen via Eha stimulated methanogenesis from formate in cell suspensions. Eha delivers electrons from hydrogen to the first reductive step in methanogenesis. Since Eha functions only anaplerotically, electron bifurcation has to function in order to provide stoichiometric amounts of electrons for this step. Eha is thought to reduce a ferredoxin that then transfers electrons to the first step in methanogenesis. We discovered two alternative pathways for reducing ferredoxins that could replace Eha. One pathway uses carbon monoxide, while the other pathway produces reduced ferredoxin from formate involving glyceraldehyde phosphate-ferredoxin oxidoreductase. In a strain where the latter pathway operates, we were able to eliminate Eha. As a potential biofuels application, this mutant provided the basis for the production of large amounts of hydrogen as well as methane from formate when a hydrogenase activity was added back. Lethality rescued by the glyceraldehyde phosphate-ferredoxin oxidoreductase pathway is a phenotype of Eha-defective mutants, enabling us to determine the genetic requirements for Eha function.

We also showed that formate limitation as well as hydrogen limitation led to decreased growth yields, and we eliminated several possible explanations for the growth yield variations. Finally, we identified genes that are required for Hmd activity.

Molecular Dissection of the *Arabidopsis* Holo-26S Proteasome

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Funding:	$180,000

PROGRAM SCOPE

The 26S proteasome is an ATP-dependent protease complex responsible for degrading many important cell regulators in plants and animals, especially those conjugated with multiple ubiquitins. It is composed of two subparticles, a 20S core protease (CP) that encloses the protease active sites and a 19S regulatory particle (RP) that binds to both ends of the CP and recruits appropriate substrates for degradation. Whereas the structure and proteolytic activities of the CP are understood at the atomic level, much less is known about the RP and the functions of its principal subunits. It has also become increasingly clear that the currently defined RP actually represents the nucleus of an even more elaborate and dynamic particle that provides multiple routes for substrate recognition. These routes may be defined by specific isoforms of individual RP subunits, the association of the RP with a host of accessory proteins, the reversible binding of target shuttle proteins, and, in the most extreme cases, by the complete replacement of the RP with alternative subparticles. Genomic analyses suggest that plants in particular exploit this heterogeneity to generate a wide array of proteasome types possibly with unique functions/specificities. The goal of this project is to better define 26S proteasome function and diversity in plants by a more complete analysis of the *Arabidopsis thaliana* particles.

FY 2012 HIGHLIGHTS

We uncovered a remarkably large number of events that affect the activity, substrate specificity, and/or abundance of the *Arabidopsis* particle. These include (1) synthesis by an integrated transcriptional regulon that measures proteasome capacity, (2) incorporation of alternative subunit isoforms that might have divergent functions, (3) capping with different regulatory complexes, (4) association with accessory proteins and target shuttle factors, (5) various post-translational modifications, and (6) an autophagic route that removes excess or aberrant proteasomes. Key to our success was the development of an affinity method to rapidly purify the particle intact that involved genetic replacement of the $\alpha 7$ subunit of the CP with a Flag epitope-tagged version. In-depth mass spectrometric (MS) analyses of the resulting preparations confirmed that the CP-RP complex is actually a heterogeneous set of particles assembled with paralogous pairs for most of the 33 core subunits. Numerous subunits were found to be modified post-translationally by proteolytic processing, acetylation, and/or ubiquitylation. MS also identified several new proteasome-interacting proteins, several of which appear to act as assembly chaperons. In addition, we detected a particle consisting of the CP capped by the PA200/Blm10 activator. Even though null *pa200* mutants are developmentally normal, a role for the PA200-CP complex in proteolysis was indirectly supported by a dramatic increase in the PA200 protein upon treating plants with the proteasome inhibitor MG132.

Engineering Selenoproteins for Enhanced Hydrogen Production

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Funding:	$165,000

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 selenocysteine 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 remain unknown.

The versatile amino acid selenocysteine is formed by the conversion of serine while attached to $tRNA^{Sec}$ resulting in selenocysteinyl-$tRNA^{Sec}$. Selenocysteine 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 selenocysteine 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.

DOE National Laboratories

Dissecting Macromolecular Regulation and Organization of Lignin Biosynthesis

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Funding:	$300,000

PROGRAM SCOPE

Lignin is one of the major plant cell wall biopolymers, representing up to 30% reduced carbon fixed by photosynthesis. Its synthesis and deposition are tightly regulated during plant growth and development, and are also in response to different environmental cues. However, our understanding of the molecular mechanism(s) underlying the regulation of lignin biosynthesis remains fragmentary, particularly, there is a dearth of information on potential post-translational regulation of the biosynthetic enzymes and proteins involved in lignin biosynthesis.

The goal of this project is to explore and dissect the post-translational modification events and macromolecular organization of lignin biosynthetic enzymes by using multifaceted strategies of biochemistry, biophysics, cell biology, and molecular genetics. Specifically, we will (1) explore and validate the protein-protein interactions of all lignin biosynthetic enzymes with their potential partners and (2) elucidate the biochemical and biological consequences of the detected interactions/ organizations, to understand metabolic interplay of lignin biosynthesis with other biological processes at posttranslational and sub-cellular levels.

FY 2012 HIGHLIGHTS

We employed a conventional yeast-two-hybrid system to search the potential interaction partners of lignin biosynthetic enzymes. *Arabidopsis* genes encoding the “soluble” enzymes PAL1 and PAL2, 4CL, HCT, CCoAOMT1, COMT1, CCR, CAD4, and the newly identified Laccase 4 (LAC4) were used as the “bait” proteins; and a normalized cDNA expressing library of *Arabidopsis* generated from the mRNAs of leaves, stems, and inflorescences of 4-6 week-old plants were ligated into the prey vector and used in the Y2H assays. Approximately 100 non-redundant primary “positive” clones were obtained and re-confirmed for the *in vitro* interactions pair-by-pair, this led us to verify about eight *in vitro* physical interaction events. Subsequently, we comprehensively characterized a plastid lipid-associated protein that was found to interact with lignin enzymes *in vitro.* We demonstrated that this protein functions in light signaling *in planta.* The physiological significance of several other interaction events is being explored.

Energetics and Structure of the ZIP Metal Transporter

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Sr. Investigator(s):	
Students:	1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$500,000

PROGRAM SCOPE

The Zrt-, Irt-like Proteins (ZIPs) are ubiquitous and conserved metal uptake transporters responsible for cellular metal acquisition. In their roles of transporting zinc, ZIPs selectively bind zinc ions and then move the bound zinc ions down an energy path across the membrane barrier. The transient zinc binding challenges the commonly held concept of zinc sites as permanent fixtures in metalloproteins. The research objective is to understand the structural basis for selective binding and energized movement of metal ions in ZIP proteins that control the zinc loading in chloroplasts. A critical technical barrier to structure analysis of plant ZIP proteins is the lack of a eukaryotic expression system for the production of plant membrane proteins in a crystallographic quantity. We have overcome this barrier using a bacterial homolog of plant ZIP proteins, termed *ZIPB*. ZIPB is the first member of the ZIP family that is accessible to x-ray crystallographic analysis. This provides a unique opportunity to explore how metal binding affinity and selectivity are built into a protein structure, and how protein dynamics may reshape metal binding sites to render mobility. We will determine the crystal structure of ZIPB by x-ray crystallography. At present, there is no structural knowledge for any zinc uptake transport protein. The ZIPB structure will fill in a critical knowledge gap. Metals are essential co-factors of photosynthetic supercomplexes in chloroplasts. The knowledge gained in the proposed research will facilitate engineering metal transport systems to overcome a critical bottleneck in biogenesis of the photosynthetic apparatus.

FY 2012 HIGHLIGHTS

An initial crystallization condition was obtained by biased sparse matrix screens. We iteratively pursued two avenues to improve ZIPB crystals: modifying the protein construct and optimizing the crystallization condition. Under an optimal condition, ZIPB grew into thin, plate-like crystals in about two weeks and then slowly transformed into 3-D like crystals over a course of six months. The chunky 3-D crystal (P2 space group, a=71.3, b=65.6, c=82.9 Å, beta=92.6 degree) diffracted beyond 3-angstrom brag spacings.

Exploration of Phenylpropanoid Regiospecific *O*-Methylation and Engineering of Novel Monolignol 4-*O*-Methyltransferases to Probe Lignin Biosynthesis

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Funding:	$450,000

PROGRAM SCOPE

Lignin is a structurally irregular biopolymer derived from oxidative polymerization of three conventional monolignols. It represents a high energy content, reduced carbon source. However, its structural complexity and rigidity prevent its direct and efficient utilization as energy feedstock and its presence in plant cell walls hinders the bioenergy applications of cellulosic fibers. Lignin polymerization requires free phenols (*para*-hydroxyls) of monolignols. Chemical modification of the phenol group of a monolignol would prevent its incorporation into the nascent lignin polymer and, therefore, reduces the quantity of cell wall lignin or alters its structure.

The overall goals of our project are to develop and adopt a protein structure-enzyme evolution-based metabolic engineering approach to explore the plasticity of lignin biosynthesis, by which we will probe the molecular and structural mechanisms of the regiospecific methylation of phenolic *O*-methyltransferases (OMTs), thereby creating a set of novel OMTs that confer strict *para*-methylation property and high specificity on particular monolignols or their analogs. Subsequently, by expressing those novel catalysts *in planta*, we will explore molecular and chemical bases for lignin polymerization and the effective solution for modulating plant lignification.

FY 2012 HIGHLIGHTS

We have created a set of monolignol *para*-methyltransferases that exhibit general substrate promiscuity and effectively etherify both monolignols for guaiacy and syringyl lignins, and we examined their effects on lignin biosynthesis in transgenic Arabidopsis. During FY 2012, we refined the structure-function analysis on the created monolignol *para*-methyltransferase variant crystallized with coniferyl alcohol, a typical monolignol; meanwhile, we conducted comprehensive analyses on transgenic Arabidopsis that expresses the created monolignol *para*-methyltransferase. We determined the content and composition of lignin and other cell wall polymers (cellulose and hemicellulose) of transgenic plants via histochemistry, conventional chemical analysis, and nuclear magnetic resonance analysis. We performed metabolic profiling on the soluble phenolics and the wall-bound phenolic esters of transgenic plants. To clarify the potential effects of expression of monolignol 4-OMT on global gene expression, we conducted cDNA microarray analysis using mRNAs from transgenic plant harboring monolignol 4-OMT. We also examined in detail the effects of down-regulation of lignin synthesis by monolignol 4-OMT on plant growth and development, cell wall biomass productivity, and the efficiency of biomass saccharification. These efforts led to a publication in *The Plant Cell*.

While analyzing Arabidopsis transgenic plants, we have also generated transgenic hybrid aspen expressing a general monolignol 4-OMT gene. In addition, to create a subset of highly substrate specific 4-OMTs to modify particular monolignols, thereby altering lignin composition and structure, we adopted a Combinatorial Active Site mutagenesis Testing strategy based on the determined MOMT crystal structure and created a set of CASTing mutant libraries. Preliminary functional screening was conducted.

Intracellular Lipid Transfer in the Biosynthesis of Photosynthetic Membranes Lipids and Storage Triacylgycerol

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Funding:	$300,000

PROGRAM SCOPE

The goal of this project is to understand the molecular basis of intracellular lipid transfer and triacylglycerol (TAG) biosynthesis in vegetative tissues of plants. Taking advantage of rich genetic resources in the model plant Arabidopsis, we initiated a simple genetic screen for novel mutants defective in lipid import into plastids and have isolated several putative mutants. We focus on two non-allelic mutants that exhibit reductions in endoplasmic reticulum (ER)-derived thylakoid lipids and also accumulate TAG in leaves. We are defining these two loci by a map-based cloning approach and determining the functional role of the encoded proteins at the molecular, biochemical, and physiological levels. These and other mutants from this screen will also provide unique tools to investigate the molecular basis of TAG biosynthesis and regulation in vegetative tissues of plants.

FY 2012 HIGHLIGHTS

We have finished the lipid mutant screen. Based on the initial genetic and biochemical analysis, eight mutants have been confirmed to be defective in lipid transfer necessary for the ER pathway of thylakoid lipid biosynthesis. Among them are mutants allelic to previously described *tgd1, tgd2, tgd3,* and *tgd4*. Two of these mutants originally named as *rtl1-1* and *rtl2-1* were characterized in great detail. The *RTL1* gene has been identified by a map-based cloning approach, and it encodes a putative membrane protein of unknown function. Detailed lipid profiling revealed that *rtl1-1* is similar to previously described *tgd* mutants. This mutant was thus renamed as *tgd5-1*. Additional analyses with two independent alleles containing T-DNA insertion mutations in the *TGD5* gene confirmed our findings with *tgd5-1*. Green fluorescent fusion and proteinase protection assay revealed that *TGD5* is localized in the inner envelope membrane of chloroplasts. Additional work was focused on the analysis of the pathway of TAG biosynthesis and its physiological significance in vegetative tissues of plants. By double mutant analysis, we found that phospholipid: diacylglycerol acyltransferase (PDAT), but not diacylglycerol (DGAT), is critical in mediating TAG biosynthesis in rapidly growing tissues such as young leaves and floral organs. Disruption of PDAT1 in the *tgd1-1* mutant background causes serious growth retardation, gametophytic defects, and premature cell death in developing leaves.

Modification of Plant Lipids

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Funding:	$1,000,000

PROGRAM SCOPE

Our overall goal is to create foundational knowledge to improve plant and microbial oils as alternative and improved energy and chemical feedstocks which will contribute to the 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 are being studied. X-ray crystallography, spectroscopy, molecular genetics, and biochemistry are employed to probe structure-function relationships within these enzymes. Specifically for the membrane class of desaturase enzymes, we are studying the oligomeric organization and its consequences with respect to metabolic channeling. For the soluble class of desaturases, we continue to dissect the mechanisms of substrate specificity and regioselectivity. We are studying the mechanisms of biochemical feedback that constrain the rate of oil biosynthesis with the goal of using this mechanistic knowledge to design biosynthetic enzymes in which the biochemical feedback is defeated. Understanding the factors that control these enzymatic transformations is allowing us to redesign lipid-modification enzymes with desired functionality. The ultimate goal of this program is to provide the knowledge base for optimizing the chemical transformations necessary for creating improved accumulation of plant lipids with desired structures in non-food crops.

FY 2012 HIGHLIGHTS

We identified residues in the fatty acid conjugase that influence reaction outcome in terms of conjugated fatty acid synthesis versus cis double bond placement; and in the course of these experiments, identified a variant that facilitates twice the conjugated fatty acid accumulation in transgenic plants. Our studies on rate limiting factors in fatty acid synthesis identified acetyl Co-A carboxylase enzyme as the target for allosteric down-regulation, and oleoyl-ACP as the molecule that binds to the ACCase and effects the negative regulation. In separate experiments, we showed that oil accumulation in Chlamydomonas reinhardtii is controlled by carbon precursor supply—not as previously thought on signals derived from diminished nitrogen supply. Consequently, we were able to define conditions that allow growth and oil accumulation simultaneously.

Quantitative Analysis of Central Metabolism and Seed Storage Synthesis

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Funding:	$500,000

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, by stable isotope metabolic flux analysis, and by 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 2012 HIGHLIGHTS

We developed a computational framework for in silico exploration of carbon allocation into different seed storage products. Based on a detailed computational model incorporating 572 biochemical reactions that play a role in central metabolism of developing seeds of oilseed rape, the goal was to predict the flux distribution in central metabolism in response to changes in storage compounds based on flux balance analysis. In particular, the biomass fractions of oil and protein measured in a seed were varied in a tradeoff fashion. The sensitivity of all reactions in the network was determined along the tradeoff. Reactions most sensitive to the tradeoff have the most potential as engineering targets. Some enzyme targets that had been suggested before in literature as relevant for oil increase, like multiple reactions of glycolysis, were identified by the method as most sensitive to oil increase. Unexpectedly, reactions related to mitochondrial respiration and ATP production were predicted to be most protein responsive, apparently since protein synthesis has particularly high demands for ATP. In addition, along with the oil-protein tradeoff, we identified distinct metabolic phases, i.e., qualitative changes in pathway usage patterns in central metabolism. These can be further explored and might be helpful in predicting and understanding regulation of the process.

Engineering Active Biological Material Interfaces with Nanotechnology

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Funding:	$986,000

PROGRAM SCOPE

The fundamental goal of this program is to tap the world of biological nanotechnology by constructing molecular-level, functional interfaces between living systems and synthetic materials. The key to domesticating life at the cellular and molecular level is communication. Living cells have tremendous ability to follow directions and perform functions on demand. In order to effectively communicate with cells, we must be able to produce synthetic materials that present the signals necessary to elicit technologically useful behaviors from cells. Progress within this program over the last funding cycle is advancing towards this goal. This program seeks to develop basic scientific understanding and synthetic capabilities to ultimately direct the behavior of cells down to the molecular level. The proposal is organized into four subtasks that breakdown roughly as follows. The first subtask emphasizes presentation of signals to cells from synthetic surfaces. The second seeks to control cells through orthogonal attachment strategies, which specifically bypass all signaling processes. The third subtask focuses on electrical interfaces with cells, both for two-way communications and direct energy harvesting. The fourth subtask includes the core optical and spectroscopic capabilities and developments that underlie much of the work. This project has been terminated, and we are in the process of wrapping up final publications.

Biological Principles of Energy Transduction: Basis for the Designed Synthesis of Molecular Catalysts

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Funding:	$500,000

PROGRAM SCOPE

The overarching goal of this research program is to understand the molecular mechanisms that allow natural protein matrices, such as hydrogenase enzymes, to control and optimize energy and charge transport. To this end, we aim to (1) understand and test how the active site geometry modulates catalytic rates and (2) clarify how the outer coordination sphere controls proton-coupled electron transfer.

FY 2012 HIGHLIGHTS

Complementary measurements using computational and experimental approaches find that changes in the positioning of functional groups in the outer-coordination sphere around the metal center result in dramatic alterations in reactivity, and suggest a mechanism to couple the reduction state of the active site metal to the surrounding protein matrix in a manner capable of controlling protein-coupled electron transport. Critical to these measurements was the development of force-field parameters that quantitatively describe the structure and motions of protein side chains in the active site and quantitative measurements that systematically measured how the position of specific protein side-chains around the active site affected the catalytic production of hydrogen.

A functional role for changes in the geometry of the cysteinate ligands bound to the metal ions in the active site of hydrogenase enzymes was identified, which is modified in different enzyme states to alter the coupling between the protein matrix and active site metal. These results suggest a means to control active site reactivity, and to efficiently mediate proton-coupled electron transfer reactions. Consistent with these results, homologous [Ni-Fe]-hydrogenase isolated from different species demonstrate a correspondence between the active site geometry, cysteinate side-chain rotation, and hydrogen production rates, where certain cysteinate arrangements around the nickel ion favorably influence hydrogenase activity.

Consistent with the proposed mechanism in the hydrogenase enzyme, the positioning of specific side chains analogous to the cysteinate ligands around the metal center (involving amide functionalities) was shown to control the reactivity (overpotential) of an active site mimic of the hydrogenase enzyme. These measurements establish an important role for the protein scaffold in the control of catalytic rates.

Separations and Analysis

Institutions Receiving Grants

Energetics of Nanomaterials	
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Sr. Investigator(s):	Navrotsky, Alexandra, California-Davis, University of Ross, Nancy, Virginia Polytechnic Inst. And State U. Boerio-Goates, Juliana, Brigham Young University
Students:	1 Postdoctoral Fellow(s), 1 Graduate(s), 1 Undergraduate(s)
Funding:	$165,000

PROGRAM SCOPE

Nanomaterials differ in structure, reactivity, and thermodynamic properties from materials in the bulk. The focus of this project continues to be the thermodynamics of nanomaterials, with synergy among three research groups: (1) Brian Woodfield and Juliana Boerio-Goates at Brigham Young University bringing expertise in nanoparticle synthesis and low temperature heat capacity measurements, (2) 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 (3) 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. In this project, such systematics are explored further with an emphasis on redox reactions and hydration. Studies of surface energies in spinel and perovskite structures are planned, and a useful set of surface energies for calculating nanoscale phase diagrams will be assembled. The details of structure and energetics of hydration layers will be probed. This fundamental understanding will be applied to two areas of technological importance: (1) iron oxide based Fischer-Tropsch catalysts for fuel production and (2) nanoporous ceramics containing alumina and titania used for catalyst supports.

FY 2012 HIGHLIGHTS

Our major discovery has been the identification of strong size-induced shifts in oxidation-reduction potentials for transition metal oxides, suggesting a new thermodynamic landscape for the transition metal oxides and their hydrated layers at the nanoscale. We have also advanced the development and understanding of our new metal oxide synthetic technique based on the solvent deficient mixing of metal salts with NH_4HCO_3. We have been able to produce a wide range of alumina and titania catalyst supports with varying pore structures and temperature stabilities as well as Fischer-Tropsch catalysts.

We have continued studies of the behavior of water on various surfaces using INS techniques in combination with heat capacity measurements. Systems of interest include titania, SnO_2 (rutile), cobalt oxides, alumina, and various iron oxides. INS spectra not only allow us to evaluate the heat capacity and vibrational entropy of the water confined on the surface of these nanoparticle systems, but also to determine the magnetic behavior of the Co- and Fe-oxides at low temperature.

Ion Production and Transport in Atmospheric Pressure Ion Source Mass Spectrometers

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Funding:	$140,000

PROGRAM SCOPE

The overall goal of the project over the past several years has been to develop a fundamental understanding of the processes that govern ion production in atmospheric-pressure ion sources and of the factors that limit transport of those ions to a mass analyzer that is operating under high vacuum. We have divided our efforts into two focus areas: (1) ion transport in inductively coupled plasma mass spectrometry (ICP-MS) and (2) ambient desorption/ionization (ADI) sources for molecular mass spectrometry.

FY 2012 HIGHLIGHTS

We have recorded fluorescence images of the cross section of a calcium ion beam in the second vacuum stage of an ICP-MS and documented changes in the profile caused by changes in the sample matrix. A high concentration of a heavy matrix species (Pb) induced a lateral shift in the beam that caused most of it to miss the entrance to the quadrupole mass analyzer. The calcium ion signal from the mass spectrometer dropped by an order of magnitude as a result of the shift.

In the area of ADI sources, we studied the effect of added hydrogen on the desorption and ionization performance of a helium plasma ADI source. The addition of 0.9% hydrogen to the helium makeup gas dramatically changed both the desorption and ionization performance of the source. Integrated ADI signals for representative test compounds increased by factors ranging from 10 to 70, and rates of desorption from the surface increased dramatically.

Optical Mass Spectrometer and Photoacoustics

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Funding:	$135,000

PROGRAM SCOPE

The first objective of this research is to investigate the capabilities of optical levitation of particles for determination of radiation force and mass measurement. A basic theory of the optical trap has been formulated and will be used to interpret measurements. Experiments are proceeding to realize a device capable of measuring radiation forces and masses of levitated objects. Second, an infrared optical pyrometer based on the photoacoustic effect has been proposed. Experiments will be conducted to test the concept of the device and to determine its capabilities, especially with regard to sensitivity. In another project, the mathematics for a photoacoustic effect excited by continuous radiation have been developed. A goal of the research is to determine if the effect can be found in experiments with a carbon dioxide laser. Last, a double resonance method for trace detection based on the use of both ultraviolet and infrared radiation has been proposed, the salient feature of which is its chemical selectivity. A goal of the research is to demonstrate the principle of double resonance in experiments.

FY 2012 HIGHLIGHTS

When a short pulse laser irradiates an optically absorbing surface, enormous thermal gradients can be produced. Theory showing the effects of large thermal gradients on photoacoustic waveforms has been completed based on a rigorous analysis of the coupled equations that describe the photoacoustic effect. High frequency, transient pressure waves are predicted as a result of the rapid heat flow caused by the thermal gradients. In experiments, a 10 ns, 532 nm beam from a Nd:YAG laser has been used to irradiate flat surfaces to produce a photoacoustic effect. The waveforms predicted by theory have been shown to exist.

The character of photoacoustic waves generated in one-dimensional phononic structures has been investigated theoretically. The photoacoustic wave production can be found from solution to an inhomogeneous Mathieu equation. New mathematical relations have been found, procedures for solution to the inhomogeneous wave equation have been developed, new travelling solutions have been defined, and the properties of the photoacoustic effect have been determined. The properties of thermal waves in sinusoidally modulated, one-dimensional structures has been investigated using the Mathieu equation with imaginary wave numbers. As well, the properties of the photoacoustic effect in two-dimensional structures and a spherical geometry have been determined. The same mathematics used in this research has been used for description of the properties of the radiation force-mass detector device presently under investigation.

Energetics of Nanomaterials

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Funding:	$110,000

PROGRAM SCOPE

Nanomaterials differ in structure, reactivity, and thermodynamic properties from materials in the bulk. The focus of this project continues to be the thermodynamics of nanomaterials, with synergy among three research groups: Brian Woodfield and Juliana Boerio Goates at Brigham Young University bring expertise in nanoparticle synthesis and low temperature heat capacity measurements, Alexandra Navrotsky at University of California-Davis brings unique capabilities in high temperature calorimetry and the measurement of enthalpies of formation and surface energies, and Nancy Ross at Virginia Tech engages 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. In this proposal, such systematics are explored further, with an emphasis on redox reactions and hydration. Studies of surface energies in spinel and perovskite structures are planned, and a useful set of surface energies for calculating nanoscale phase diagrams will be assembled. The details of structure and energetics of hydration layers will be probed. This fundamental understanding will be applied to two areas of technological importance: iron oxide-based Fischer-Tropsch catalysts for fuel production and nanoporous ceramics containing alumina and titania used for catalyst supports.

FY 2012 HIGHLIGHTS

At present, there are no measured surface energies for a major group of oxides, namely perovskites. Toward this, we worked on measuring the surface energy of SrTiO3 and CaTiO3. Thus far, we have successfully synthesized nanoparticles of various crystallite sizes of SrTiO3 and CaTiO3 by hydrothermal technique followed by annealing at different temperatures; these were also characterized by XRD. The surface area and the water content in the nanoparticles were determined employing BET and a thermogravimetry test. In a view to measure the surface energy of hydrated SrTiO3, the enthalpy of dissolution of SrTiO3 of different crystallite size have been determined by drop solution calorimetry into molten 3Na2O.4MoO3 at 973 K. The obtained enthalpy of drop solution have been corrected for its water content to get the surface energy of anhydrous SrTiO3, being measured by water adsorption calorimetry. In the next period, we have to measure the surface energy of CaTiO3 and other perovskites of different cation sizes in order to investigate the effect of cation size and distortions on surface energies.

DC to Daylight: Local Spectroscopies for Subnanometer Spatial Resolution Chemical Imaging

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Funding: $210,000

PROGRAM SCOPE

The research objectives of this project are to develop broadly applicable, local imaging spectroscopies based on the scanning tunneling microscope (STM) for the microwave, infrared, visible, and near-ultraviolet ranges. All of these measurements give insight into molecular/assembly function that are beyond the typical purview of scanning probe microscopies. We combine simultaneous measurements of structure, function, and spectra with sub-molecular spatial resolution.

FY 2012 HIGHLIGHTS

After demonstrating regioselective photoreactions of pairs of molecules inserted in self-assembled monolayers, we have succeeded in measuring the intrinsic photoconductances of molecular dyad and triads that are designed for organic photovoltaics.

We have developed special nanohole array substrates to enhance local and far-field spectra. We have used these in combination with STM measurements (on the same substrates) to get statistically significant distributions of optical function, such as photoisomerization. We are expanding these measurements further to new families of molecules, and are exploring how the arrangement and precise assembly of molecules leads to changes in their switching and reaction efficiencies.

Computer Simulation of Proton Transport in Fuel Cell Membranes

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Funding: $170,000

PROGRAM SCOPE

This project involves a unique multiscale computer simulation methodology for studying proton solvation and transport in proton exchange membranes (PEMs). A key component of the project is a novel atomistic molecular dynamics (MD) simulation approach called the Self-Consistent 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. Methodological and algorithmic advances and enhanced code scalability allow the SCI-MS-EVB simulations to access increasingly large system sizes and long simulation times. Key results already obtained have revealed the remarkably complex behavior of the proton solvation and transport in the hydrophilic domains of Nafion, including a an unusual and unexpected anti-correlation between vehicular transport and hopping transport. A new mesoscopic-scale simulation method for proton transport in PEMs is also being developed, including a multiscale bridging of the atomistic SCI-MS-EVB data to the mesoscopic proton transport modeling, in turn coupled to complex PEM morphology. Applications of the overall multiscale simulation approach are underway for PEMs such as Nafion^{TM}, as well as for other target PEMs with enhanced proton conductance properties.

FY 2012 HIGHLIGHTS

The mesoscopic simulation method has provided a significant new connection with measurements from experiments. The method relies on combining a coarse-grained (CG) model for the PEM with a smoothed-particle hydrodynamics (SPH) description of the proton concentration diffusion. The combined CG-SPH method provides a foundation for exploring the mesoscale regime for proton conduction that lies beyond atomistic approaches, but at a higher degree of spatial and time resolution than traditional engineering calculations of transport properties.

Atomistic SCI-MS-EVB simulations for three of the main morphological models of Nafion currently proposed in the literature were also performed. These three morphological models included the lamellar structure, the cylinder model, and the cluster-channel model. Each structure was studied at a series of hydration levels, and the spacing between the interfaces of the hydrophilic and the hydrophobic regions was varied to explore the geometric factors affecting proton solvation and transport. The results show qualitatively different proton transport mechanisms are occurring as the size of the water domain is changed in the different morphological models, and so a detailed analysis of the transport mechanisms was carried out.

Fluoropolymers, Electrolytes, Composites and Electrodes

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

PROGRAM SCOPE

The overall objective of this research program is to provide new fluoropolymer electrolyte membranes and carbon composite/fluoropolymer electrolyte catalyst support materials for use in electrochemical energy conversion devices, particularly polyelectrolyte membrane fuel cells (PEMFCs). Fluoropolymer materials have exceedingly high chemical/thermal stability, which is essential in applications such as PEMFCs that involve long-term exposure of materials to harsh environments. This research program seeks to exploit longstanding technical expertise at Clemson in fluoropolymer synthesis (Clemson has the only operating academic laboratory in the United States outfitted for safely working with hundred-gram quantities of tetrafluoroethylene) to provide advances in basic understanding of how fluoropolymer ionomers behave and how new fluoropolymer ionomers may be designed, synthesized, and used to help solve problems in electrochemical energy storage and conversion.

The research program is organized into four topical areas as follows: (1) low equivalent weight (EW) perfluoro-sulfonimide (PFSI) ionomers, (2) telechelic perfluoro-cyclobutyl (PFCB) ionomers, (3) mesoporous nanocomposite carbon supports for use in PEMFC electrodes, and (4) electrospun PFCB mats for use in PEMFC stacks. The research seeks to produce membranes having high ionic conductivity and good dimensional stability, and also carbon composite support materials having high mixed ionic/electronic conductivity over a wide range of conditions, including high-temperature/low-humidity conditions that normally cause diminished protonic conductivity.

FY 2012 HIGHLIGHTS

Progress has been realized in all four topical areas, and ongoing work continues towards achieving program goals. Of particular note is work from two publications (one published in *Langmuir* and one in *Chemical Communications*) on the preparation of carbon-based electrocatalyst supports having mixed electronic/ionic conduction. The Langmuir paper describes creation of mesoporous carbon composite materials designed to have zirconia-based anchoring sites suitable for binding phosphonates end-groups in telechelic fluoropolymer ionomers. The Chem Comm paper describes synthesis of the telechelic polymers and their combination with carbon/zirconia composites to produce mesoporous materials having ionomer coatings throughout the full interior texture of the material. This work provides large steps forward towards the rational preparation of mixed electronic/ionic conducting materials for use in fuel-cell electrodes.

Imaging of Conformational Changes

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Funding:	$223,361

PROGRAM SCOPE

Our ultimate objective is 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, 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.

Mapping Non-Covalent Surface Functionality Using Single-Molecule Probes

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Funding:	$247,648

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 will be 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 2012 HIGHLIGHTS

A new chemical imaging technique for surfaces, MAPT (Mapping using Accumulated Probe Trajectories) was developed. In MAPT, a time series of images is obtained using single-molecule TIFRM and image processing is used to determine the locations of all the individual molecules adsorbed to the surface. By tracking these locations through a time series, physical properties of probe/surface interactions (such as adsorption rates, local diffusion, desorption probability and surface coverage) are determined. The use of single molecule localization makes the MAPT analysis intrinsically super-resolution, and we have demonstrated resolution of ~100 nm in our un-optimized initial results. MAPT can be used on any surface and provides absolute and quantitative values of physical interaction properties. Homogenous surfaces can then be characterized and used as “calibration” points to connect small-scale heterogeneities to specific surface chemistries. This technique was used to directly connect local surface chemistry with dynamic molecular behavior on heterogeneous surfaces, leading to new understandings of: (1) “crawling” versus “flying” modes of molecular surface diffusion, (2) anomalously long surface residence times and anisotropic protein diffusion on crystalline regions of nanostructured melt-drawn polyethylene, and (3) aggregation of proteins at the oil-water.

In other research, we developed a variant of single-molecule tracking based on dynamic single-molecule resonance energy transfer, that permits us to make direct connections between the conformation (e.g., end-to-end distance) of individual molecules and their dynamic behavior at nanometer and micron length scales. We also studied the dynamic molecular behavior of hydrophobic probe molecules on a homologous series of surfaces that exhibit subtle differences in hydrophobicity. In another series of experiments, we are developing probes that are sensitive to local surface charge. Finally, studies are underway using single molecule resonance energy transfer to map active catalytic sites.

Nanophotonic and Atmospheric Pressure Ion Production in Imaging Mass Spectrometry

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Funding:	$145,000

PROGRAM SCOPE

Driven by continued analytical challenges, there is a major interest in the development of new ion sources for mass spectrometry. This project aims to significantly expand the application of mass spectrometry to the direct analysis of biological, environmental, and security-related samples through two new types of ion sources. Motivated by our results in ultratrace analysis by photonic ionization based on silicon nanopost arrays (NAPA), we study the direct ion production from microorganisms. This enables a new direction toward the integration of biological systems with nanofabricated structures for mass spectrometric analysis. Direct metabolic imaging of biological systems with mass spectrometry is also enabled by laser ablation electrospray ionization (LAESI). Based on the promising preliminary results, we expand this technique to a broader array of sample types and improved spatial resolution. Integration of ion mobility separation (IMS) into the system is expected to enhance the metabolite coverage. These two new techniques provide information on the chemical composition within a single cell that has implications for the understanding of cell metabolism, division, disease states, and ecological effects. Cells of the same type exhibit diverse metabolic makeup depending on their phase in the cell cycle, history, and interaction with the environment. We apply LAESI mass spectrometry in combination with optical fiber-based ablation to interrogate single cells for their metabolite composition.

FY 2012 HIGHLIGHTS

Single yeast cells with volumes as low as 30 fL are deposited and directly analyzed on NAPA. During LDI, laser excitation of the posts ruptures the cell, exposing the intracellular components, and ionizes them for detection by mass spectrometry. As a result, 24 metabolites, corresponding to 4% of the known yeast metabolome, are detected. We also studied the effects of oxidative stress on the metabolism of yeast at the single cell level. To enhance the ionization of non-polar compounds in LAESI, we introduced a hot gas jet into the ion source. This simple modification enabled the simultaneous ionization of diverse groups of chemicals. This summer, the implementation of the LAESI ion source in combination with IMS was completed. The produced mass spectra exhibit over 1,100 peaks, a significant improvement over the ~300 peaks observed without the IMS. In the coming period, we will utilize this enhanced performance for mass spectrometric imaging and single cell analysis.

Precisely Tunable High Performance Carbon Molecular Sieve Membranes for Energy Intensive Separations

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Funding: $120,000

PROGRAM SCOPE

The overarching goal of this work is development of an improved fundamental framework to guide the systematic understanding and formation of carbon molecular sieve membrane materials appropriate for important energy intensive separations. Determination and analysis of the effects on penetrant sorption and transport properties caused by systematic variations in precursor polyimide structures and pyrolysis protocols will be key thrusts of the work. Moreover, effects of aging on the performance of asymmetric hollow fibers formed from attractive polymer precursors will be investigated. A diverse but systematic set of dianhydride and diamine monomers will be used to explore effects of matrix rigidity and packing of precursor polyimides on final carbon properties. Evaluation of sorption enthalpies and activation energies for diffusion of the resultant carbons in terms of van't Hoff and Arrhenius models will be used to understand thermodynamic vs. kinetic factors contributing to separation. We will further analyze diffusion selectivites in terms of activation energies and activation entropies to improve the understanding of discrimination on the basis of shape of the penetrants. We expect entropic factors to be particularly important for challenging olefin-paraffin pairs where differences in diffusion can provide significant advantages to compact olefins vs. the slightly more bulky paraffin analogs. Complementary studies will be used to gain additional insights into evolution of structures during the systematic formation work. Single gas, binary and ternary mixtures will be considered over a range of temperatures and at pressures up to 80 atm. A special focus will be upon the interaction of pyrolysis temperatures and pyrolysis atmospheres. This aspect of the work will expand upon an important recent discovery by our group that the presence of parts-per-million levels of oxygen enables exquisite control of permeability and selectivity in carbons.

FY 2012 HIGHLIGHTS

We have obtained one of the two key monomers that we have proposed to add to our program, "asymmetric 3,3',4' -biphenyl dianhydride" (a-BPDA), to add to the diversity of structures we will investigate. After some difficulties, we finally got a supplier from outside the U.S. and are performing analyses to determine its purity. We continue to pursue a second specialty monomer, "asymmetric 2,3,3' ,4' -benzophenone dianhydride" (a-BTDA), which has proven even more difficult to obtain. While we can synthesize the material if there are no other options, we are trying to avoid this for the sake of efficiency. While we are pursuing this last monomer, we have successfully synthesized several polymers using the more conventional "symmetric 3,3',4,4' -biphenyl dianhydride" (s-BPDA) monomer with Diaminomesitylene (DAM) and (4,4'-hexafluoroisopropylidene) diphthalic anhydride. We have also transformed the precursors into carbon molecular sieve membranes and are in the process of testing them.

Binding Anions Selectively With Modular Triazolophanes and Releasing them With Light

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Funding:	$125,000

PROGRAM SCOPE

The goals of this project are to (1) investigate the fundamental properties of shape-persistent receptors for selectively recognizing large anions and (2) 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). We will synthesize rigid receptors to elaborate the effect of size, shape, and electrostatic complementarity on selective binding to polyatomic anions: cyanide, azide, thiocyanate, perchlorate, and perrhenate. Binding affinities between various anions and specific receptors will be measured to determine selectivities, and any differences between the selectivity will be understood with the aid of theoretical modeling. A series of photo-driven receptors will be designed and synthesized that employ photoswitches like azobenzene and stilbene to modulate the conformations of the receptor. The receptors will be furnished with noncovalent contacts (e.g., π stacking and hydrogen (H) bonds) to define good and bad binding cavities.

FY 2012 HIGHLIGHTS

We have been investigating how the strategic positioning of Coulombic and H-bonding interactions within a well-defined cavity can allow selective binding of polyatomic anions. A series of elliptical macrocycles bearing differing electrostatic potential surfaces have been synthesized. These planar receptors display rigid cavities that are expected to bind linear anions (N_3^-, SCN^-) with high affinity on account of size and shape matching. In addition, the stepwise synthesis of these receptors allows for electrostatic tuning of the receptor's cavity by incorporating pyridyl H-bond acceptors. These intracavity lone pairs are expected to enhance binding of anionic guests bearing H-bond donors ($H_2PO_4^-$, HSO_4^-). Progress towards the elucidation of the binding selectivities and evaluation of the hypotheses is ongoing.

We have designed a foldamer with an azobenzene cap to effect the binding of Cl^- ions in mixed aqueous solutions, which are the most competitive environments in which to perform molecular recognition. We have evidence of a mechanism used every day by proteins yet rare in synthetic chemistry, wherein hydrophobic interactions are shown to stabilize and partially organize a foldamer to extract hydrophilic chloride ions from increasingly aqueous solutions. Therein, a double helix gains stability upon burial of ~80% of the π surfaces creating a potent H-bonding microenvironment. The chloride's binding affinity to the duplex is substantial in 25% water in acetonitrile ($\log \beta_2 = 12.6$), and instead of decreasing, it remains strong even as the water content is raised to 50% ($\log \beta_2 = 13.0$). With the rise in predictable designs of abiological foldamers, this water-assisted strategy can in principle be utilized for binding other hydrophilic guests.

Elucidation and Reduction of Interference Effects in Inductively Coupled Plasma Spectrometry

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PROGRAM SCOPE

The principal goal of this project is to understand more fully the reasons and mechanisms for so-called matrix interferences in inductively coupled plasma (ICP) spectrometry and, through this better understanding, to devise methods for recognizing and overcoming the errors. In this context, a sample matrix is anything besides the sought-for species (the "analyte"). Unfortunately, the sample matrix influences the strength of emission or mass-spectrometric signals that arise from the same concentration of an analyte. As a result, the signal from, say, calcium will change depending on whether the calcium comes from chalk, bone, or limestone.

The approach we are using to solve this problem is to map the concentrations and behavior of species intrinsic to the plasma and those added to the plasma with the sample. Methods include Thomson scattering, Rayleigh scattering, computed emission tomography, and saturated laser-induced fluorescence. Species being mapped include argon excited states, atom and ion ground-state and excited-state populations, electron concentrations and energy distributions, and various temperatures (electron, ionization, excitation, and gas-kinetic).

FY 2012 HIGHLIGHTS

We have recently devised a foolproof strategy to recognize situations in which matrix interferences exist in ICP emission spectrometry. Because the ICP is spatially heterogeneous, the severity of a matrix interference changes from one plasma location to another. Indeed, even with a fixed analyte and interferent concentration, the effect can change from a signal enhancement in one location to a suppression in another. The flagging method is then straightforward: a calibration curve (emission intensity vs. concentration) is created at a number of spatial locations in the ICP by using a series of solutions of known concentration. The emission signal from an unknown sample is then obtained at each of those locations and its apparent concentration determined at each location by reference to the corresponding calibration curve. If the sample behaves in the same way as the standards, the determined concentrations will be the same for all spatial locations. If the determined concentrations differ, a matrix interference clearly exists.

We are using this same approach to identify plasma locations where the interference is either absent or minimized. The method has been applied to conventional radial (side-on) plasma viewing and to the recently popular axial (end-on) viewing mode and also to samples that are aqueous or organic solutions. So far, the method appears to be universally applicable.

Molecular-Level Investigation of Diffusion Behaviors within Cylindrical Nanoscale Pores

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Funding:	$240,000

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 will be obtained from self-organized materials, such as surfactant-templated mesoporous silica (STMS) and cylinder-forming block copolymers (CFBCP), and employed as model systems. Mass transport will be investigated using single-molecule fluorescence techniques, including single molecule tracking (SMT) and fluorescence correlation spectroscopy (FCS), as well as ensemble techniques. The molecular-level mechanisms reflecting the molecule-nanopore interactions will be directly probed by single-molecule methods, which will lead to better understanding of ensemble mass transport behavior acquired from identical nanopores. The results will reveal key molecular-level mechanisms governing the rate and selectivity of ensemble molecular behavior within nanopores that can be directly linked to the properties of nanoporous media employed in chemical separations and catalysis, and as membrane separators in fuel cells and batteries. The comprehensive understanding that will be obtained will lead to more accurate predictions of the performance of newly developed nanoporous materials in their energy-related applications, and will facilitate the engineering of nanoporous media optimized for these applications. We will also pursue new experimental approaches as means to overcome certain fundamental limitations of diffusion studies based on existing fluorescence techniques. 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 to assess microscale domains with differently oriented nanopores in STMS films and also to reveal flow-induced alignment and diffusion pathways in rod-shaped block copolymer micelles.

FY 2012 HIGHLIGHTS

We have reported a shear-flow method to prepare highly-aligned surfactant mesophases in microfluidic-channels (A. W. Kirkeminde, et al. *J. Phys. Chem. B* 2011, *115*, 12736.) and employed this method to prepare STMS monoliths comprising cylindrical nanodomains having a very high degree of nanopore orientational order (S. C. Park, et al. *J. Phys. Chem. B*, in press.). We have discovered that directional penetration and evaporation of 1,4-dioxane induces millimeter-scale alignment of cylindrical domains in polystyrene-poly(ethylene oxide) diblock copolymer (PS-*b*-PEO) films (K.-H. Tran-Ba, et al., *J. Phys. Chem. Lett.* 2012, *3*, 1968.). We have developed the means to prepare self-organized nanoporous anodic oxide from metallic gallium (B. Pandey, et al., *Langmuir* 2012, *28*, 13705.). These achievements have been made using SMT and our orthogonal regression methods.

Hyper-thin Membranes for Hydrogen Purification

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Funding:	$140,000

PROGRAM SCOPE

This research is divided into two parts. In the first part, a fundamentally new surface modification method will be developed for converting hydrophobic surfaces, in general, and poly[1-(trimethylsilyl)-1-propyne (PTMSP), in particular, into ones that can support polyelectrolyte multilayers formed via the layer-by-layer deposition method. Because of its unique microporous structure and its high permeability, extensive use will be made of PTMSP as support material for fabricating asymmetric membranes containing hyperthin (i.e., <<100 nm) permeation-selective, polyelectrolyte multilayers. In the second part of this research, structurally matched polyelectrolytes will be synthesized and used to fabricate hyperthin membranes. It is expected that the use of identical polymer backbones will minimize polymer-polymer incompatibilities and result in enhanced miscibilities and higher permeation selectivities relative to unmatched analogs.

FY 2012 HIGHLIGHTS

A major development that has come out of the studies during this past contract period has been the discovery of unexpected barrier properties of structurally matched and unmatched polyelectrolyte multilayers. Specifically, we have found that hyperthin (14 nm) polyelectrolyte multilayers formed from poly(diallyldimethylammonium chloride) and poly(sodium 4-styrene sulfonate) (PSS) deposited onto PTMSP supports exhibit exceptionally high CO_2/N_2 permeation selectivities, ranging from 100-150. We have also discovered that structurally matched analogs, which were prepared from poly(4-vinylbenzyltrimethylammonium chloride) and PSS, show similar selectivities with permeances that were two to three times greater. Although the H_2/CO_2 permeation selectivities with these membranes were only modest, their exceptionally high CO_2/N_2 permeation selectivities suggest that such materials have potential for the separation of CO_2 from flue gas, which is the largest contributor of man-made CO_2 to the atmosphere.

Self-Assembled Ionophores and Membrane Active Transporters

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Funding:	$310,000

PROGRAM SCOPE

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 and dynamics of self-association and ion binding, (2) designing self-assembled ionophores that selectively bind various ions, and (3) constructing supramolecular structures that function as synthetic ion channels.

FY 2012 HIGHLIGHTS

(1) Supramolecular Assemblies that Transport Ions across Phospholipid Bilayer Membranes. We recently prepared a novel synthetic ion channel that can move ions across phospholipid bilayer membranes. Such transporters could eventually serve as intracellular sensors or antimicrobial agents. We achieved the desired properties by attaching guanosine groups to the ends of a lithocholic acid dimer. This study is, to the best of our knowledge, the first experimental demonstration that G-quadruplexes can be used as synthetic ion channels. We are currently trying to determine the transport mechanism and develop improved analogs.

(2) New Cl- Anion Receptors/Membrane Transporters. We extended our use of self-assembly to prepare compounds that transport Cl- and HCO_3 anions across bilayer membranes. Using liposomes, we compared the H+/Cl- co-transport activity and the Cl-/HCO_3- anion exchange properties of a series of synthetic molecules and natural products (prodigiosins and ceramides). Their ability to transport Cl- and HCO_3- at micromolar concentrations, their low molecular weight, and their simple preparation make these compounds lead platforms for building new approaches toward selective ion separations.

Graphene Membranes with Tunable Nanometer-Scale Pores

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Funding:	$150,000

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 objectives of this work are 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 to 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 2012 HIGHLIGHTS

Since the project started in July 2012, we have built and tested a diffusion cell apparatus to measure relative permeabilities of different ions across graphene membranes. We have performed preliminary experiments in which pores were created in graphene and have observed indications of selective ionic transport using the diffusion cell. An apparatus has also been fabricated for measurement of ionic currents through small areas of graphene membranes.

Chemical Microscopy of Conjugated Macromolecular Systems: Fundamental Design Strategies for Nanoscale Photonic Antennae and Networks

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Funding:	$129,000

PROGRAM SCOPE

The focus of this project is to develop new materials and methodologies for understanding directional control of energy and charge flow in conjugated nanomaterials. Current emphasis is on the study of crystalline nanoscale assemblies (1D nanoparticles and 2D nanowires) of different semiconducting polymers, and the connection between polymer chain packing and exciton coupling within single polymer chains and between co-facially ordered chains. The analytical methodologies developed within this program will enable a more detailed understanding of the connection between polymer morphology and packing structure with photophysical observables, which will ultimately lead to design strategies for directional control of energy and charge flow in nanostructured polymer systems.

Separations of Stable Isotopic Ions in Homogeneous, Highly Charged Nanopores

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Funding:	$160,000

PROGRAM SCOPE

This project aims at controlling the size and surface charge of membrane nanopores to develop a unique mechanism for the separation of ions that have small differences in their mobilities, with a long-term goal of separating stable isotopes. Development of models of transport in nanopores is also important for emerging micro and nanofluidic applications. In nanofiltration through negatively charged pores or polyelectrolyte films on a membrane surface, selective exclusion of cations gives rise to a streaming potential due to momentarily selective transport of anions. This potential subsequently accelerates cation transport and slows anion transport to give zero net current. Importantly, the streaming potential will have the greatest effect on ions with the highest mobility, so anions with lower mobilities will selectively pass through the membrane. A similar principle applies to separation of cations using membranes that exclude anions. The initial research in this project focuses on separating alkali metal cations; but with sufficient control over pore size, the concept may allow isotope separations based on small mobility differences. Streaming potentials can also lead to negative rejections (the concentration is greater in the permeate than in the feed) of trace ions. In this case, the potential pulls the trace ion across the membrane at rates higher than convection. Such negative rejections present an intriguing possibility for both separating and concentrating trace ions. All of these separations rely on control over membrane chemistry and geometry at the nano and macromolecular scales.

FY 2012 HIGHLIGHTS

Negatively charged nanopores in track-etched membranes allow selective passage of Li^+ over Cs^+ with minimal pressure drops. Li^+ rejections are 20%, and the Li^+/Cs^+ selectivity is around 3.5. Positively charged nanopores allow similar separations of acetate from Br^-. These results confirm the mechanism of selective transport in nanopores. Polyelectrolyte films deposited on porous supports show Mg^{2+} rejections around 95%; but remarkably, rejections of trace K^+ from the same solutions are negative at 200%. The amount of K^+ in the permeate is 3 times that in the feed, demonstrating that negative rejections can concentrate trace ions.

Interfacial Solvation Under Aggressive Conditions

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

PROGRAM SCOPE

The goal of this project is to develop molecular-level insights into the dynamics that occur within polymeric membrane architectures when they are operated under viable H_2 purification conditions. Toward this end, we create well-defined monolayer architectures (single component and mixtures) and adjust the position of probe molecules and cross-link sites, and then determine the picosecond interfacial dynamics across a wide range of fluid densities and compositions.

These experiments provide information on the internal dynamics within these membranes under realistic operating conditions, and they are helping to guide how best to develop platforms that are more/less prone to swelling and failure.

FY 2012 HIGHLIGHTS

We have developed a high-pressure total internal reflection fluorescence apparatus for measuring monolayer interfacial dynamics between 250 and 380 K up to 500 bar with picosecond time resolution. We have used this device to determine the effects of (1) terminal residue ($-CH_3$ vs. $-CF_3$) and CO_2 fluid density on the rotational reorientation dynamics of “short” dansylated propylsilane monolayers; (2) chain length, surface loading, and CO_2 fluid density on the rotational reorientation dynamics of dansylated alkylsilane monolayers; (3) cosolvents (MeOH, EtOH, H_2O) (1 mole%) on membrane internal dynamics; and (4) cross-linking strategies.

In the next period, we will extend these efforts to thicker film systems (100-400 nm) and more elaborate fluid mixtures, explore bottle brush platforms, and implement tip enhanced Raman scattering spectroscopy to image the film chemistry with sub wavelength resolution.

Coordination-Chemistry-Derived Materials Featuring Nanoscale Porosity and Selective Chemical Separation

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Funding: $220,000

PROGRAM SCOPE

The 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 (e.g., alkane/alkene, xenon/krypton, etc.).

FY 2012 HIGHLIGHTS

(1) A key development, has been the use of computational modeling to discover new MOFs or identify existing MOFs showing potentially superior chemical separation capabilities. Subsequent experimental syntheses have confirmed the effectiveness of the approach. The computational approach provides a means for evaluating many more candidate materials than could ever be examined experimentally.

(2) There has been considerable uncertainty and controversy over whether BET analyses of gas sorption (a standard technique for mesoporous materials) accurately report on internal surface areas for ultra-microporous (pore diameters below 0.7 nm) MOF materials. We simulated nitrogen and argon isotherms in MOFs and zeolites having ultra-micropores and used the simulated isotherms as pseudo-experimental data to evaluate the BET method for these structures. BET surface areas calculated from the simulated N_2 and Ar isotherms agree well with the accessible surface areas obtained directly from crystal structures in a geometric fashion. However, this is only true when the BET analysis was performed using the appropriate pressure range based on published consistency criteria; the BET analysis underestimates the surface area if it is done in the “standard” BET pressure range.

(3) A third result we wish to highlight is the discovery of emergent collective behavior by propylene in various M-MOF-74 compounds, resulting in exceptional thermodynamic selectivities for separation of propylene and propane (e.g., S = 46 at 1 bar, with higher values anticipated at higher pressures).

Molecular Aspects of Transport in Thin Films of Controlled Architecture

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Funding:	$155,000

PROGRAM SCOPE/FY 2012 HIGHLIGHTS

Understanding and control of molecular transport in nanoscale structures is a problem of considerable continuing interest that is critical to numerous energy-related technologies, including energy storage, membrane separations, and environmental remediation. The ultimate goal of our program is to establish intelligent control of molecular transport in space and time at small length scales—enabling the construction of materials and structures that can sense molecular characteristics (e.g., size, charge, molecular shape, etc.) and then generate signals that control transport based on those characteristics. Based on an understanding of transport and reactivity in nanoscale architectures, structures capable of manipulating molecular entities with unprecedented control are being pursued.

This project focuses on two objectives. The first is an understanding of the complex factors that govern transport under conditions of confinement and crowding in nanoconfined spaces. Fluorescence correlation is being used to study translational and rotational dynamics of model systems in single nanopores under electrokinetic (EK) flow where the degree of confinement and molecular crowding can be systematically varied. In addition, wide-field imaging is used to study the reaction dynamics of single enzymes confined within zero mode waveguides, a system which allows exquisite control over the degree of molecular crowding. We are currently studying how the zero mode waveguide structure may be used to study single electron transfer reactions. The other objective is to study electrochemical and catalytic reactions in the confined geometries represented by model nanocapillaries. Heterogeneous electron transfer and surface-directed enzymatic and non-enzymatic catalysis reactions are studied in special architectures, where the chemical reaction is directed to occur at a specific location. In order to model ultraefficient reactions, we are studying the coupling of an upstream electrolysis reaction at a nanoband electrode to downstream catalytic consumption of the reagent. These systems are studied in both planar and vertically integrated geometries, giving rise to tight coupling of electron transfer to electrokinetic flow. These experiments have required the development of new chemical analysis capabilities to characterize chemistry occurring within a buried nanopore, where the products are not physically accessible.

In summary, work in this project advances toward optimal utilization of nanoscale structures by developing fundamental understanding of the coupling of transport and reactivity at the nanoscale, that supports the application of nanoporous structures to problems in energy storage, membrane separations, and environmental remediation. These experiments are producing fundamental new knowledge and enhancing our understanding of how transport and reactivity are coupled in systems that are crowded, confined, or both.

Chemical Imaging with Cluster Ion Beams and Lasers

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Funding:	$209,070

PROGRAM SCOPE

This renewal proposal to the Department of Energy concerns 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 C_{60} or Ar_{2500} molecules, that is focused to a well-defined point on the target. During the energy deposition process, both neutral and ionized molecules are desorbed from the surface. This research is aimed toward finding novel ways to ionize the neutral molecules using 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 2012 HIGHLIGHTS

A new high field femtosecond IR pulsed laser system for photoionization of sputtered molecules via a tunneling mechanism has been implemented in the laboratory. During the past year, the lab has focused upon optimizing the parameters of this laser system, including intensity, wavelength, and polarization, to minimize photofragmenation and reduce multiphoton excitation. Several target molecules have been successfully characterized, including cholesterol, b-estradiol, and a variety of other lipid molecules. Preliminary images have been acquired from Algae cells optimized for possible energy production. During 2012, the PI was given the American Chemical Society award for Analytical Chemistry, and a symposium was organized at the Philadelphia ACS meeting highlighting research of relevance to this DOE award. The preliminary results have been presented at a SIMS workshop and at the ACS meeting. The first publications resulting from the implementation of this new laser system are currently being prepared.

A Physicochemical Method for Separating Rare Earths: Addressing an Impending Shortfall

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Funding:	$150,000

PROGRAM SCOPE

Renewable energy applications such as wind turbine generators, and hybrid- and electric vehicles require high-purity rare earth materials. China currently produces ~97% of rare earths globally. To develop alternative sources and diversify the supply chain, there is a clear need for new chemistry that reduces the cost and environmental toll of the industrial-scale separations. The goal of this project is to separate certain high-value rare earths based on their unique physicochemical properties. We are developing new organo-nitroxide compounds that we expect will be element-specific extractants for rare earth ions. Through coordination of the redox active nitroxides at rare earth ions, we expect to trigger intermediate metal valences through the emergence of strong intra-molecular electron correlations. In the course of the project, we will prepare new nitroxide ligands with varied electronic properties. We will prepare metal complexes of the nitroxides and evaluate their electronic, magnetic, and spectroscopic properties in order to detect and quantify signatures of intermediate valence. We will use ligand substituents to tune the relative ligand energetics and understand the electronic requirements for the emergence of intermediate valence. We will apply this information to develop optimized nitroxides for use as extractants in liquid-liquid separations of rare earth ions.

FY 2012 HIGHLIGHTS

We have refined and expanded the synthetic chemistry, electrochemistry, and electronic structure calculations using DFT on a family of organo-nitroxides for use as ligands and/or extractants in rare earths chemistry. We have also shown the nitroxides bind La, Ce, Pr, and Tb ions effectively. We have interrogated the electrochemistry and electronic spectroscopy of the Ce complexes. We have established the formal oxidation state and valence of the central member of this series as truly tetravalent using XANES spectroscopy in collaboration with Dr. Corwin Booth, LBNL. The series of cerium congeners that have been prepared exhibit unprecedented reducing Ce(III)/Ce(IV) redox events. We have developed a semi-empirical correlation using DFT-calculated electron affinities for the complexes and their electrochemical data. We are currently extending this correlation in an effort to predict and isolate Pr-nitroxide complexes.

Electrohydrodynamic Tip Streaming

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

PROGRAM SCOPE

When subjected to strong electric fields, liquid drops and films form conical tips and emit thin jets from their tips. Such electrohydrodynamic (EHD) tip streaming or cone-jetting phenomena, which are sometimes referred to as electrospraying, occur widely in nature and technology. Well known examples of cone-jetting include ejection of streams of small charged drops from pointed tips of raindrops in thunderclouds and the popular technique of electrospray mass spectrometry. More recently, EHD cone-jetting has emerged as a powerful technique for direct printing of solar cells. Currently, electrosprays either find use or are being considered for utilization in a growing number of areas, including electric field-driven extraction, micro- and nano-particle production, and encapsulation for controlled release. Motivated by applications in separations (electric field-driven extraction), analysis (electrospray mass spectrometry), and energy (drop-wise printing of solar cells), one of the main goals of this research program is to develop a fundamental understanding of the temporal development of EHD tip streaming phenomena.

It is now well known that a pendant or a sessile drop that is subjected to an electric field elongates in the field direction and ultimately becomes unstable at a turning point in field strength. Upon loss of stability, an EHD tip streaming jet is emitted from the conical tips of such drops. *What happens, however, if a pendant drop is connected to a sessile drop through a cylindrical hole in a plate from which a pendant drop hangs and a sessile drop protrudes?* A sessile drop that is connected to a pendant drop through a liquid filled cylindrical hole having the same radius as the radii of the bases of the two supported drops is known as a double droplet system (DDS) or a capillary switch (CS). Such systems can be used in optical applications as adaptive liquid lenses and as fluid or particle “grabbers” in analytical chemistry. The statics of such systems are now well understood; and study of their dynamics, albeit in the absence of electric fields, is a developing area. However, even a rudimentary understanding of the EHD of such systems is currently lacking.

FY 2012 HIGHLIGHTS

We have demonstrated definitively that EHD tip streaming is a universal phenomenon in that the size and charge of droplets in an electrospray are independent of whether the droplets are emitted from a film or a free drop. Furthermore, we have shown that the emitted droplets are Coulombically stable at the time they are created and that there is a universal scaling law relating droplet charge to the charge carried by a drop at the Rayleigh limit of stability. Electrospray droplets can undergo further breakup, or explosions, upon evaporation and/or coalesce with other droplets. For uncharged droplets coalescing in air, we have uncovered that the conventional picture of coalescence is incorrect in that a regime that describes the initial dynamics of coalescence has heretofore been missed.

Preparation of Chemically Functionalized Surfaces through Ion Soft Landing and their Utilization in Heterogeneous Reactions

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Funding:	$162,000

PROGRAM SCOPE

This project expands the capabilities of surface preparation methods by utilizing gas-phase ions as chemical reagents to modify surfaces. Specific preparation methods include ion soft landing (SL), wherein intact gas phase polyatomic ions are deposited onto surfaces, and reactive ion/surface collisions. Traditionally, SL experiments are performed in high vacuum where limited ion currents do not allow for bulk material preparation; but surface modification is still possible. A goal of this research is to expand ion SL to ambient conditions where higher ion fluxes and bulk material preparation are possible. It is desirable to efficiently focus ions in air for ambient surface preparation; and, when combined with multiplexed sources, it is feasible to produce higher ion currents. The ultimate goal of this project is to understand mechanistic relationship between ion/surface collisions under vacuum and in the ambient air, tailor surfaces with desirable chemical properties, and modification of alkanes via nitrogen fixation to prepare high value derivatives.

FY 2012 HIGHLIGHTS

Systematic studies of vacuum SL and ion/surface reactions have been completed using a previously built instrument with in-situ surface characterization methodologies: secondary ion mass spectrometry (SIMS) and surface enhanced Raman spectroscopy (SERS). The combination of SIMS and SERS proved useful to characterize the charge state of such deposited ions as methyl orange. Analysis by in situ SIMS and SERS suggested that the soft landed methyl orange ion exists in the neutral form.

Ambient ion SL was scaled up by focusing ions in air using an elliptical DC lens system. The ellipse allows for plate/surface separation of several cm, while maintaining 70% efficiency into a 1 cm^2 area compared to 15% without focusing. Silyation chemistry has been studied under conventional solution-phase conditions, in vacuum and in ambient ion. Ambient silyation chemistry has been achieved by reacting alcohols with silyl ethers in an electrospray plume. Carbon-carbon bond functionalization was demonstrated by placing heavy alkanes on filter paper cut to a point to which keV potentials were applied in a nitrogen environment. This led to products with C=N bonds, which can be collected on a surface and characterized with mass spectrometry and Raman spectroscopy. Mechanistic questions remain about the nature of the nitrogen reagent and if it will be possible to scale the reaction up using multiple paper tips. A multiplexed spray source was designed and combined with a moving stage, and the system is currently being evaluated for increased ion currents. It will soon be used to soft/reactively land chosen ions onto particular surfaces to provide fundamental understanding of ion/surface chemistry in air.

The Dynamics and Thermodynamics of Gaseous Macro-ions

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Funding:	$374,000

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. Progress in this work leads to improvements in mass spectrometry as a tool for the structural characterization of molecules relevant to energy development and consumption. 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 2012 HIGHLIGHTS

Two new functional-group specific reaction types have been discovered, which relate to the first specific aim mentioned above. One involves the selective gas-phase modification of carboxylic acid functionalities via carbodiimide chemistry. The other involves the alkyl esterification of carboxylate groups via alkyl ion transfer from quaternary ammonium cations. An ion trap mass spectrometer has been modified to allow for operation at ion trap temperatures of 233-423 K. A UV laser has been procured and is being interfaced with the temperature controlled ion trap. This tool will be used to study the ion/ion chemistry of cluster ions as well as to photodissociate ions that have been tagged with a chromophore via ion/ion chemistry. This work relates to the second specific aim mentioned above. An ion spectroscopy instrument has been constructed that allows for the photodissociation of ions cooled to roughly 10 K. Initial studies have been performed with model chromophore-containing systems, such as tryptophan. This work relates to the second specific aim mentioned above.

Combinatorial and High Throughput Membrane Synthesis and Testing: Tailoring Membrane Surfaces to Applications

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Funding:	$325,000

PROGRAM SCOPE

The goals of this 3-year research project are to (1) study the mechanism atmospheric pressure plasma-induced graft polymerization (APP) on poly(ether sulfone) (PES) membranes; (2) test, screen, and select the best performing (i.e., with respect to protein fouling, protein sieving, and membrane permeability) vinyl monomers from a large library of commercially available monomers using high throughput methods; (3) expand the monomer library using hypermodern combinatorial chemistry methods; and (4) investigate the mechanisms of protein-resistance using Quartz Crystal Microbalance with Dissipation Monitoring.

FY 2012 HIGHLIGHTS

During the first year of this renewed grant, we have demonstrated that APP can effectively graft monomers and induce polymerization on PES membranes, synthesized our first set of 10 monomers using combinatorial chemistry, shown that three have excellent protein resistance, and used Hanson parameters to help explain the behavior of the 10 monomers.

Combinatorial methods offer opportunities to expand the chemical space of monomers for protein-resistant (or anti-fouling) membrane surfaces. A series of amide monomers were synthesized from vinyl chloride and amine compounds with different functional groups. These newly synthesized amide monomers were used to modify commercial PES membranes by high throughput atmospheric pressure plasma. After challenging these membranes with BSA (static fouling), the PES membrane surfaces grafted with N-(3-hydroxypropyl)methacrylamide (A3), N-(4-hydroxybutyl)methacrylamide (A4), N-(4-hydroxybutyl)methacrylamide (A6), N-(3-methoxypropyl)methacrylamide (A7), N-(2-(dimethylamino)ethyl)-N-methylmethacrylamide (A8), and N-(2-(diethylamino)ethyl)-N-methylmethacrylamide (A9) were analyzed for protein-resistance. A4 and A7 modified PES membranes exhibited both lower fouling and higher permeation flux when compared with the control membrane; and their performance was comparable with previously identified best monomers, PEG- and zwitterionic- grafted PES membranes. After challenging membranes with a BSA filtration assay (dynamic fouling), A3 and A7 modified PES membranes exhibited the highest average permeability; these membranes could be useful for BSA purification from blood (large industrial separation challenge). The A10 modified PES membrane showed the highest selectivity and could be useful for removing BSA from other permeable blood components. Structure-property analysis from the Hansen Solubility Parameters was predictive for experimental measurements and thus revealed the importance of surface-water interactions for reducing protein fouling.

Nanoporous Membranes for Hydrogen Production: Experimental Studies and Molecular Simulation

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Funding:	$160,000

A summary for this program was not available at press time.

Separation of Highly Complex Mixtures by Two-Dimension Liquid Chromatography

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Funding:	$120,000

PROGRAM SCOPE

Solving complex scientific challenges requires both a multidisciplinary approach drawing on and extending current knowledge and the application of advanced technology. By combining knowledge about metabolism with expertise in separation science, we intend to develop a means to enable production of energy from a natural source.

The solution of many problems encountered in biochemistry requires the combination of separation methods far more powerful than those currently used and of advanced methods of identification of the separated compounds. Conventional methods use unidimensional chromatography, which cannot provide the separation power that is necessary to resolve sufficiently the thousand compounds found in metabolomic samples and to allow their identification by mass spectrometry. This last method can identify only a limited number of compounds coeluting at any given time. We propose to apply multidimensional chromatography, which separates on a second column the fractions eluted from a first one operating with a different phase system, and to analyze on-line the eluate of the last column with mass spectrometric detection, in order to study the metabolism of some monocellular algae with a view to develop a natural energy supply. The samples examined will be fractions of metabolites extracted from several strains of these microorganisms.

FY 2012 HIGHLIGHTS

Work done during the previous grant period used a cyanobacteria, *Botryococcus braunii*, chosen from a list of algae suggested by DOE as having a high yield in lipid production. Its dry biomass may contain up to 40% of lipids or more. Significant information on the behavior and physiology of this species is available. We obtained limited but promising data on the lipid metabolism of this species. It produces large amounts of long linear alkyl alcohols or carboxylic acids that have properties similar to those of the hydrocarbons used to power diesel engines. We plan to separate the metabolites involved in the synthesis of these compounds by combining the results provided by different combinations of two-dimensional chromatography and mass spectrometry. Once these metabolites are known, it should be possible to correlate their concentrations and the production rate of lipids usable in diesel fuels. Based on the outcome of this study, similar knowledge could be acquired for different species of algae and this knowledge could permit other scientists to modify their genome and accelerate their metabolism in order to establish an economic natural source that uses solar energy to convert carbon dioxide into diesel fuel.

Development of Ionization Methods and Structural Imaging MS

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Funding:	$170,000

PROGRAM SCOPE

This project is directed toward the development of advanced mass spectrometry (MS)-based methodologies and techniques for characterization of complex molecules. The research focuses on two areas: (1) ionization techniques that permit selective and efficient ionization of analytes, and (2) development of rapid, high-throughput tandem MS and ion mobility-mass spectrometry (IM-MS) that yield high quality ion structure information. Nanoparticles (NP) and nanorods (NR) are used to selectively capture analytes, which are analyzed by laser desorption ionization (LDI) MS. The general strategy utilizes Ag and Au NP or NR functionalized with organic molecules that have hydrophobic-hydrophobic or hydrophilic-hydrophilic interactions with the analyte of interest. Using this strategy, we have successfully performed LDI of both small molecules and macromolecules using much longer laser wavelengths, 800-1064 nm.

The Achilles' heel of MS is that many molecules exist as isomeric species having the same m/z value and oftentimes similar, if not identical, mass spectra. On the other hand, it is not uncommon for isomeric ions to have very different sizes (shapes) which yield very different ion-neutral collision cross sections and/or different ion-neutral interaction potentials; thus, IM-MS can be used to separate isomeric forms. Much of our IM-MS research emphasizes development of new and better strategies for IM-MS, i.e., increasing the separation resolving power and overall instrument sensitivity, and enhancing ion structure determinations. We recently showed that the IM-MS resolution performed at low temperatures (80 K) is ~ 4 times greater than that performed at 300 K, in excellent agreement with theory.

FY 2012 HIGHLIGHTS

We have developed two new NP LDI-MS sensors: (1) a sol-gel doped impregnated AuNP that selectively captures fatty acids and lipophilic analytes, and (2) an AgNP impregnated polyvinylpyridine polymer (PV4P) that can be tailored for selective capture of a broad range of organic functional groups. Adding the transition metal ions Fe^{3+} and Mn^{2+} to the PV4P controls the selectivity. We have developed novel IM-MS capabilities employing collision-induced dissociation (CID) and electron-transfer dissociation (ETD) that greatly simplify tandem MS of multiple-charged ions generated by ESI. In this experiment, mass-selected analyte ions are subjected to CID (or ETD) and the product ions are dispersed on the basis of size-to-charge by ion mobility and by m/z using TOF-MS. The experiment is thus denoted as ESI-MS-

CID (or ETD)-IM-MS. The data obtained in this manner are plotted using a 3-D format (ion abundance, size-to-charge, and m/z), and all ions of the same charge fall on distinct trendlines. The individual trendlines can be extracted and plotted as conventional mass spectra, thereby greatly increasing (10-20x) S/N ratios and reducing (10-20x) chemical noise. These enhanced instrument capabilities broadly impact research in the areas of petroleomics, plant and microorganism lipidomics, and imaging MS.

Fundamental Structure/Property Studies of Gas Separation Membrane Polymers

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Funding:	$155,000

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. To achieve this goal, we are investigating a platform of polymeric materials known as thermally rearranged (TR) polymers, which are synthesized through a solid-state reaction of *ortho*-functional polyimides. These polymers exhibit state-of-the-art separation performance for certain gas separations, such as CO_2 removal from natural gas. However, little is known about the mechanism of transport that endows these materials with such excellent transport properties. Furthermore, little is known about how these materials will perform for other separations.

FY 2012 HIGHLIGHTS

We published two papers describing gas permeability, solubility, and diffusivity in an *ortho*-functional polyimide and TR polymers prepared from 3,3’-dihydroxy-4,4’-diamino-biphenyl (HAB) and 2,2’-bis-(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA). As HAB-6FDA is reacted from a polyimide to a TR polymer, gas solubility of H_2, N_2, O_2, CH_4, and CO_2 increases by a factor of approximately 2 to 3. However, gas diffusivity increases by over an order of magnitude for all of these gases. Therefore, the beneficial transport properties for TR polymers are mainly a result of high gas diffusivity.

To take advantage of these diffusivity effects, we are undertaking a two-part structure/property study. First, we have investigated the change in gas permeability for TR polymers synthesized from polyimides with various *ortho*-functional groups. These *ortho*-functional groups react and leave during thermal rearrangement. By increasing the molecular size of these groups, we have shown that bulkier leaving groups lead to higher gas transport properties for TR polymers synthesized from the same nominal backbone structure. Second, to identify new materials with high gas diffusivities, we have synthesized new polyimide and TR polymer materials. To date, we have synthesized 32 materials.

Separations and Analysis using Bipolar Electrodes

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Funding:	$151,000

PROGRAM SCOPE

Our goals for the current project period are to understand how bipolar electrodes (BPEs) (1) are able to achieve separation and enrichment (focusing) in a multi-channel format and (2) to demonstrate that BPEs are effective for highly parallel electrocatalyst screening. Moreover, we have combined our BPE focusing experiments with advanced simulations carried out by our collaborator, Prof. Ulrich Tallerek (Philipps-Universität Marburg, Germany). These studies have advanced our previous understanding of the fundamental principles of bipolar electrochemistry and opened the door to new and exciting areas. A key advantage of BPEs is that they require no direct electrical connection to operate, as they are powered through an externally applied electric field. This means they are readily amenable to large scale screening methods, as well as low-powered separations.

FY 2012 HIGHLIGHTS

We achieved several important milestones. First, we showed for the first time that by changing the direction of electroosmotic flow in a microelectrochemical device, a BPE can be used to enrich cationic species. Furthermore, a single BPE connecting two separate microchannels can be used to separate and enrich anions and cations simultaneously. This is possible because of the unique nature of the enhanced electric field produced near a BPE. We have also demonstrated that charged analytes can be selectively gated from one microchannel to another by BPEs. The region of depleted charge near an operating BPE provides an electrophoretic barrier, preventing analyte movement and allowing an enriched band to be selectively guided into another channel.

BPEs can be used to simultaneously analyze the thermodynamics and kinetics of electrocatalytic reactions on large numbers of candidate materials. We demonstrated this principle by screening the electrocatalytic properties of numerous combinations of different metals for the oxygen reduction reaction (ORR). This approach has a number of advantages over others that have been reported. (1) BPEs require no direct electrical connection; and, therefore, very large arrays of electrodes can be screened simultaneously. (2) Individual BPEs within an array can be selectively and rapidly modified using a simple robotic spotter. (3) A single, simple DC power supply and a microscope are the only equipment required to record screening data. In addition to these experimental advances, we are also developing computational tools to rapidly evaluate data obtained using this new method.

Analytical Spectroscopy Methods for Liquid/Solid Interfaces

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Funding:	$140,000

PROGRAM SCOPE

Liquid/solid interfaces play a key role in many aspects of energy-related chemistry, including separation steps in chemical analysis and materials processing, surface interactions in heterogeneous catalysis, and the behavior of charged or dipolar species molecules at electrically polarized interfaces. As a result, there is a significant need to understand chemical structure, transport, and reaction kinetics at interfaces between liquids and solids. This program is aimed at developing new spectroscopic imaging methods for analysis of chemical structure and kinetics at these interfaces. In particular, confocal Raman microscopy is being applied to determine the chemical composition of interfacial species and their evolution in space and time within single porous particles. This experiment is also being adapted to single-particle, solid-phase extraction to enable rapid, ultra-trace level Raman scattering detection in small volume samples. The kinetics of molecular transport and binding to surfaces are being characterized by single-molecule fluorescence imaging, to understand their role in chemical separations and the time response of separations and sensors. Finally, changes in interfacial molecular populations and chemical structure in response to electrical potentials are being characterized by surface-enhanced Raman scattering and single-molecule imaging. Small potentials applied to conductive surfaces are used to manipulate the structure and properties of the interface, to change interfacial populations of ions, and to control interactions with analytes in solution, yielding sensors with controllable selectivity.

FY 2012 HIGHLIGHTS

We have successfully employed surface potential control to control the assembly of ordered monolayers on metal surfaces, monitoring the structural evolution of the layer by surface-enhanced Raman spectroscopy. Charged macromolecules at interfaces were fluorescently labeled and imaged as single-molecules, while their surface populations were controlled by applied potential. In this next funding period, we are applying fluorescence imaging to observe the trajectories of single molecules within porous, chromatographic particles to better understand transport phenomena that govern solute retention and separation efficiencies. A new correlation strategy for faster imaging of these processes is currently in development. Confocal Raman microscopy of solutes that accumulate within individual C18-modified porous silica particles is being developed into a uniquely sensitive tool to obtain vibrational spectra of very low concentration (10 nM) hydrophobic solutes in aqueous solutions. We are presently investigating the kinetics of solute accumulation to understand both the speed of response and the nature of transport of hydrophobic molecules within chromatographic particles.

Flotation Chemistry of Nonsulfide Minerals

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Funding:	$135,000

PROGRAM SCOPE

The overall goal of this flotation chemistry research program is to provide a basis for improved separation efficiency in nonsulfide mineral flotation by establishing the fundamental features of collector (surfactant) adsorption reactions and the nature of the corresponding hydrophobic surface state. In this way, appropriate surface chemistry control strategies are being developed for the more efficient use of mineral resources. At the present time, surface chemistry research includes study of phyllosilicate minerals and salt-type minerals, particularly rare earth (RE) minerals, as well as consideration of water film stability and collector disposition at mineral surfaces.

FY 2012 HIGHLIGHTS

In the case of phyllosilicate minerals, attention is being given to the anisotropic surface charge and wetting characteristics of kaolinite and chlorite. Significant progress has been made with the development and utilization of AFM procedures to examine 500 nm kaolinite particles and describe the chemistry of their face and edge surfaces. Of particular significance is the experimental demonstration that the two face surfaces of kaolinite differ significantly with respect to surface charge and wetting characteristics. These results have been presented at professional society meetings and published in archival journals. In addition, AFM research continues with the surface chemistry of chlorite and other layered silicates. Procedures have now been developed to prepare and analyze edge surfaces of such structures. The AFM measurements are being complemented with electrokinetic measurements, surface spectroscopy analysis, and molecular dynamics simulation to describe the nature of particle interactions and collector adsorption.

The surface chemistry study of salt-type minerals is directed at the analysis of interfacial water structure in order to explain the flotation behavior of selected minerals. Electrokinetic measurements, surface spectroscopy analysis (SFVS), and molecular dynamics simulation are being used for different surfaces including the surfaces of fluorite (CaF_2), halite (NaCl), and sylvite (KCl). Based on the analysis of interfacial water structure and collector adsorption, conditions for the hydrophobic surface state are explained. Of particular significance is the study of the strategic rare earth minerals. Already samples of bastnasite (Ce, La, Y) CO_3F, have been prepared and experiments are in progress to describe the fundamental surface properties of importance in the design of improved flotation technology for the recovery of rare earth resources. Based on initial efforts, a paper has now been accepted for publication.

Results from this fundamental research program have been and are being used to develop new flotation strategies for our mineral resources including the processing of low grade bauxite ore, the recovery of potash and other soluble salt minerals, and the beneficiation of phosphate ore. It is expected that similar contributions will be made in the development of improved flotation technology for the processing of domestic rare earth mineral resources.

Energetics of Nanomaterials

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Sr. Investigator(s):	
Students:	1 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$80,000

PROGRAM SCOPE

The objective of this proposal is to develop understanding and predictive systematics for the thermodynamic properties of nanomaterials and their anhydrous and hydrated surfaces and to apply such knowledge to systems of importance to technology. The proposal brings together three groups—Brian Woodfield at Brigham Young University, Alexandra Navrotsky at University of California-Davis, and Nancy Ross at Virginia Tech (VT)—to study oxide nanoparticles from synthetic, thermodynamic, and structural points of view. The VT group is working with researchers at neutron facilities to use inelastic neutron scattering (INS) methods to study the molecular vibrations of water adsorbed onto the surface of oxide nanoparticles. Neutrons are highly sensitive to scattering by hydrogen atoms and much less sensitive to scattering from the metal oxides, and thus provide the ideal probe to explore hydration layers of nanoparticles. These experiments not only provide information about the structure and dynamics of water confined on the surfaces of oxide nanoparticles, but they also allow one to calculate the heat capacities and entropies of the hydration layers from the vibrational density of states (VDOS) determined by the INS experiments. In addition, neutrons provide an ideal method to explore the magnetic properties of nanomaterials which may differ from their bulk properties. These studies provide an atomic scale understanding about the energetics and stabilities of nanoparticles, which will be useful for the technological development of metal oxide nanoparticle systems.

FY 2012 HIGHLIGHTS

We have explored PdO, alumina, and iron oxide nanomaterials with neutrons. PdO-based nanoparticle systems have been extensively studied due to their interesting and varied chemical and physical properties; and we have demonstrated that the degree of water coverage of the PdO particles subtly influences the heat capacity and vibrational entropy of the hydration layers [Spencer et al., J. Chem. Thermodynamics (2012)]. We have also studied alumina (Al_2O_3) nanoparticle materials which are highly porous metal oxides with accessible three-dimensional (3D) surface areas that have been widely used in catalysis, energy technologies, and environmental remediation. Our INS studies are being analysed to elucidate the structure and thermodynamic properties of the water confined on these 3D surfaces and will be the first study of this kind. We will continue our studies of iron oxide nanoparticles, which are not only an inherent part of the environment but are also useful in many technological applications. We have measured INS and completed an extensive analysis of nano-hematite Fe_2O_3. This study was conducted on SEQUIOA at the SNS, and preliminary results (IPTS-4774) clearly indicate a pronounced size effect on the magnetic properties of these particles. With further INS experiments, we will explore the interplay of particle size, hydration level, and magnetic properties of iron oxides.

DOE National Laboratories

Separations and Analyses (Chemical Analysis of Nanodomains)

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Sr. Investigator(s):	Fang, Ning, Ames Laboratory Petrich, Jacob, Ames Laboratory
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Funding:	$600,000

PROGRAM SCOPE

The objective of this research is to develop far-field spectroscopy and microscopy techniques that outperform existing technologies for the analysis of phenomena that occur in nanoscale spatial regimes, focusing on polymer films, ionic liquids, and phenomena at the solid/liquid interface. Many important phenomena occur on a spatial scale that is smaller than can be probed noninvasively by conventional optical spectroscopy and microscopy techniques, such as polymer domains in biosensors, fuel cells, batteries, photovoltaic devices, light emitting diodes, and thin film transistors. The function of these devices requires molecular domains with varying properties, including domain sizes spanning below the diffraction limit to the macroscale.

Our sub-diffraction imaging techniques break the limit imposed on traditional imaging techniques and open the possibility of achieving non-invasive, ambient pressure measurements of phenomena that occur in the tens of nanometer spatial scale. The analysis techniques employed are primarily based on stimulated emission depletion (STED), total internal reflection (TIR), or nanoparticle probes. Ultimately, the developed methods and measurements fill the Basic Energy Science aim to characterize nanoscale materials, which will lead to new routes for manipulating and assembling them and, ultimately, for developing new and revolutionary energy technologies.

FY 2012 HIGHLIGHTS

A total of 17 research papers were published in peer reviewed journals by this program during the 2012 Fiscal Year.

STED: A supercontinuum STED microcope for sub-diffraction spatial resolution fluorescence lifetime imaging was described; and to further the utility of the instrument, non-blinking quantum dots were demonstrated to be a stable fluorescence tag for STED imaging with superior signal-to-noise properties compared to the small molecule tags that had been used up to this point. The non-blinking quantum dots were synthesized by our collaborator in the Homogeneous and Interfacial Catalysis in 3D Controlled Environments program.

TIR: Scanning angle surface plasmon resonance and plasmon waveguide resonance Raman spectroscopy were demonstrated for the first time, and both formats were subsequently used to measure thickness and composition of thin polymer films. Raman spectroscopy was performed to measure the monomer composition of a complex polymer in a heterogeneous environment. Finally, high-precision tracking was demonstrated with 10-nm spatial resolution using automated scanning angle total internal reflection fluorescence microscopy and the non-blinking quantum dots described above for our STED work.

Nanoparticle Probes: Several advances were made with our nanoparticle assisted technologies, including 3D high precision tracking of plasmonic nanoparticles using differential interference contrast and total internal reflection scattering microscopies.

Separations and Analyses (Mass Spectrometric Imaging of Plant Metabolites)

Institution:	Ames Laboratory
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Funding:	$195,000

PROGRAM SCOPE

The research objectives are to develop mass spectrometric imaging (MSI) technologies to spatially map metabolite distributions within plant tissues. We are using these techniques to address specific biological questions concerning the differential distribution of metabolites among diverse cell-types, and to dissect metabolic regulatory processes. Such imaging technology is of particular importance in multicellular organisms, such as plants, to identify and characterize cooperative and antagonistic genetic interactions, as well as environmental modifiers that asymmetrically regulate the complexity of plant metabolism. This imaging analytical capability is being developed in the context of understanding plant metabolic processes that impact the collection and storage of solar-energy in the form of energy-dense biochemicals.

The project is using MSI technology we developed to address biological questions associated with specialized metabolism that is asymmetrically distributed among discreet cellular-sized structures. The choice of systems is guided by three criteria: (1) focus on metabolism leading to the biosynthesis of energy-dense molecules (i.e., molecules composed primarily of carbon and hydrogen, lacking oxygen); (2) use the current resolution power of the imaging technology (~12 µm resolution) to visualize metabolites and metabolism to the level of about a single plant cell; and (3) take advantage of the team’s expertise in the biochemistry and genetics of acetyl-CoA metabolism.

FY 2012 HIGHLIGHTS

Significant achievements where accomplished in three different categories: (1) improvements to enhance the spatial resolution of the MSI technology, achieving single cell level spatial resolution of 12 µm; (2) improvements in the mass-resolution to enhance the chemical identification of analytes; (3) use of multiplexed MSI scheme to reduce the time-required for data acquisition; and (4) integration of MSI technology into functional genomics analysis of genes required for the biosynthesis of energy-dense biochemicals.

Laser Materials Interactions (Ablation)

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Funding: $350,000

Chemical analysis has grown to become a critical component of our world, from the safety of children's toys to nonproliferation. Laser ablation has become the most promising approach for direct solid sample chemical analysis. Benefits include no sample preparation, no chemical waste from digestion, real-time measurements, stand-off capabilities, and reduced exposure to hazardous samples. Laser ablation provides a "green technology" approach to the traditional acid digestion infrastructure for analysis. Every sample can be ablated. In principle, the concept is simple: a high-power pulsed laser beam explodes a small portion of any sample (solid, liquid, gas) into a plasma plume, and subsequent analysis is performed by optical or mass spectrometry. However, all laser ablation applications are based on empirically established parameters; accurate models do not exist to describe fundamental mechanisms. This research endeavors to elucidate underlying laser ablation processes for chemical (elemental) analysis at atmospheric pressure. Mass spectroscopy, emission spectroscopy, and imaging are utilized to study ablation processes; and the data from these studies are related to fundamental models. Interferometric and Schlieren imaging with femtosecond time resolution are utilized to measure ablation plume properties, including electron, vapor, and particle ejection processes.

Fundamental Studies of Novel Separations

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Mahurin, Shannon, Oak Ridge National Laboratory
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Funding: $850,000

PROGRAM SCOPE

The overall goal of this project is to investigate fundamental issues of chemical separation phenomena at the gas-solid, and gas-liquid interfaces of nanostructured architectures and unconventional separation media that selectively bind or transport target molecular species via tailored interactions. To achieve this goal, we will pursue three specific aims: (1) *How can we rationally control porosity and functionality of novel carbon materials for advanced gas transport?* (2) *How can we achieve high selectivity and facile release of targeted gas molecules by designing and synthesizing smarter liquid systems?* (3) *How can we control the interaction of gas molecules with advanced separation media by switchable external stimuli?* To control the porosity and functionality of porous carbons, we will explore novel charged liquid precursors which introduce desired pore size and chemical functionality for improved separations. Advanced gas transport will be enabled by novel membrane configurations based on porous carbons. To achieve high selectivity and facile release of targeted molecules, we propose to make smarter ionic liquids based on the "catch-and-release" concept where easily reversible adducts are formed between target gas molecules and a functional solvent instead of binding the two together permanently. Another strategy involves the pursuit of ionic liquids which provide stronger solvation of targeted gas molecules beyond conventional non-bonded interactions (e.g., H-bonding, induced dipole, and acid-base interactions). External stimuli such as optical and electric fields provide an easily switchable mechanism to reversibly modulate the local environment of a solvated molecule. We propose the invention of photo-switchable ionic liquids to control the strength of "solvent" interaction with gas molecules, and the use of modulated electrical double layers to tune the interaction of a gas molecule with the cations and anions of an ionic liquid supported in a porous carbon, as new strategies to control the sorption and release of target gases. In answering these specific aims, we will also be addressing three major issues of extraordinary importance in separations crucial to the DOE mission: mass transport, selectivity of interactions, and release mechanisms.

FY 2012 HIGHLIGHTS

A general strategy for the synthesis of porous triazine-framework-based membranes with intrinsic porosity was developed by superacid catalyzed trimerization of aromatic nitriles. This new class of porous polymer membranes with tunable functionalities and porosities significantly expands the currently limited library of intrinsically porous polymers/membranes for gas separation.

Using molecular simulation, we investigated the effect of nitrogen doping on the adsorption capacity and selectivity of CO_2 versus N_2 in model mesoporous carbon. We showed that nitrogen doping greatly enhances CO_2 adsorption capacity due to the preferred interaction between CO_2 and the electronegative nitrogen. This work indicates that nitrogen doping is a promising strategy to create mesoporous carbons for high-capacity, selective carbon capture.

Improving Chemical Separations through Understanding Weak Interactions in Condensed Phases

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Funding:	$400,000

PROGRAM SCOPE

The goal of this research is to provide an improved understanding of the relatively weak molecular-level interactions in solution that drive the affinity and selectivity between target ions and receptors in chemical separations. We will expand the currently limited information available on the specific contributions of solvation environment to selectivity to form the basis for new predictive capability. Experimental and modeling work in this project will continue to be informed by, and contribute to, advances in understanding of fundamental interactions through separations experiment, liquid-phase spectroscopy, and *ab initio* modeling studies. We will focus on the specific aims of determining local structure of anions and receptors in solution and correspondingly understanding changes in entropy in solvation and binding through molecular-level models. To accomplish these specific aims, we will take advantage of newly-available capabilities in neutron scattering and computational sciences at ORNL.

Success in this research will enhance the molecular-level predictability of extractive separations by explicitly considering solvation effects and will contribute directly to Department of Energy missions in energy production and utilization, environmental remediation, and subsurface energy applications, and to national and energy security.

FY 2012 HIGHLIGHTS

Isotopically-substituted neutron scattering experiments were carried out on KNO_3 in D_2O on the NOMAD diffractometer at the Spallation Neutron Source to provide new information on the local solvation of nitrate ion in aqueous solution. New results for the bound coherent scattering length difference between ^{16}O and ^{18}O found previously in this program were used along with substitution of ^{14}N with ^{15}N to give two distinct views of local structure. While the results are currently being analyzed along with X-ray total scattering data, it is clear from these experiments that NOMAD offers a new capability for resolving local structural information from isotopic-difference data which is needed to differentiate enthalpic and entropic contributions to the free energy of ion solvation.

Molecular dynamics predictions of scattering experiments have demonstrated the value of null-water experiments (in H_2O + D_2O mixed solvent) in deconvoluting the complex local structure of anion solvation. These calculations were a key factor in the success of a proposal for beam time on NOMAD for studies of chloride-ion hydration in concentrated $CaCl_2$ solutions. These measurements of structure near chloride ion are expected to add new detail to the current understanding of hydration of the chloride ion, extending to high salt concentrations where solvation shells are expected statistically to be incomplete.

Principles of Chemical Recognition and Transport in Extractive Separations

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Funding:	$1,170,000

PROGRAM SCOPE

The overarching goals of this program are to understand the factors underlying selectivity in the separation of ions by novel receptors and to learn how such factors can be manipulated by design to yield predictable behavior. A unified thrust targets anion recognition in particular. Three key questions are being addressed: (1) *Can unprecedented anion selectivity be obtained by theory-based design of host architectures bearing shape- and size-complementary arrangements of electropositive groups?* (2) *Can molecular building blocks containing appropriate binding groups be made to self-assemble into functional anion receptors with predetermined selectivity?* (3) *What is the contribution of coulombic or ion-pairing interactions to the selectivity of anion receptors, and how can these effects be harnessed in cooperation with other donor interactions?* The corresponding program incorporates state-of-the-art computations to guide synthesis of new anion receptors and precursors for self-assembly based on hydrogen-bond donor interactions. Precisely designed self-assembled receptors are being pursued, including metal-organic cage receptors, covalent polyhedral cages, and new covalent organic frameworks. Ion-pairing effects are probed through study of new ditopic receptors plus novel synergized anion-exchange systems. Resulting transformative understanding of the theoretical, structural, and thermodynamic principles underlying anion recognition strongly support DOE needs in its nuclear fuel-cycle, environmental-cleanup, national-security, and energy missions.

FY 2012 HIGHLIGHTS

Principles controlling the recognition of ion pairs were delineated by characterizing self-assembling crystalline and liquid-liquid systems in which ditopic receptor sites were shown to accept both cations and anions simultaneously. The results indicate that enhanced selectivity can be obtained by providing for binding of ion pairs rather than single ions in separation systems. In other studies, a symmetry-based set of principles was developed for the first time to provide a comprehensive basis for the design of molecular organic frameworks.

Research in Advanced Chemical Measurements Technology

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Funding:	$580,000

PROGRAM SCOPE

The objective of this program is to provide an understanding for control of the ultrafast energy flow in nanoparticles and their reactions by imaging individual nanoparticles with chemical contrast and nano-scale spatial resolution. Sample heterogeneity provides contrasting nanoparticles for study. Our approach is linear, nonlinear optical, and time-resolved spectroscopy as a means to probe important nanoparticles and their interfaces where chemical changes occur. Interrogation of individual nanoparticles highlights the optical, electronic, dynamic, and reactivity differences between particles due to different size, morphology, and structure. The scientific questions we wish to answer include the following. (1) *Can we monitor surface reactions of individual nanoparticles to then discover means to control those reactions*? (2) *Can we prepare unique nanoparticle structures by assembly of individual particles or by the conscious incorporation of defects where tailored energy transport properties result*? (3) *Can we understand excitonic energy transport within heterogeneous, polymeric nanostructures of photovoltaic interest using two-photon echo and pump-probe spectroscopy*? Answers to these questions will have a profound influence on surface chemical analysis and interfacial chemistry. New fundamental chemical understanding of interfacial processes will lead to design of new materials with transformational properties to impact important DOE mission areas such as solar energy conversion, electric energy storage, and catalysis for energy.

FY2012 HIGHLIGHTS

We have studied the surface chemistry of an important, environmentally-friendly semiconductor - ZnO. A single nanowire was probed with 100 nm spatial resolution using laser second harmonic generation during exposure to carbon dioxide and water vapor. Thin alumina coatings slowed down the carbonate formation but did not prevent it. We have also studied ultrafast dynamics in two classes of candidate solar energy harvesting materials. First, exciton dynamics in copper-phthalocyanine (CuPc) single crystal nanowires were probed using femtosecond pump-probe spectroscopy. Our observation of long-lived excitons and their diffusive motion along one-dimensional molecular stacks makes these nanowires particularly suitable for photovoltaic applications. Second, a picosecond time-resolved fluorescence study of water-soluble polythiophene derivatives showed that the electronic excited-state dynamics depend strongly on temperature and side-chain length. Highly ordered polymer chains in the aggregates that are formed above certain temperatures were suggested.

Sampling, Ionization, and Energy Transfer Phenomena in Mass

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Students:	2 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$1,140,000

PROGRAM SCOPE

The overarching goal of this research is to advance the capacity of mass spectrometry (MS), in combination with other imaging modalities, to study and characterize with nanometer spatial resolution molecular constituents of surfaces under real world conditions. Advanced and unique mass spectrometry-based investigative techniques are used and studied to provide an improved understanding of chemical and physical processes ongoing at interfaces to advance areas like photovoltaic cells, Li-ion battery electrodes and solid-electrolyte interface, catalysis, block co-polymer systems, biomass recalcitrance and productivity, and chemical sensor systems that are critical in the Department of Energy (DOE) energy research and national security missions. Specific aims in this work are to understand and implement the means to efficiently ablate, desorb, or extract surface species and then efficiently collect and transport at atmospheric pressure (AP) the neutrals or subsequently the ions created, with emphasis on micro- and nanoscale liquid extraction, thermal desorption, or laser ablation/desorption approaches to surface sampling with molecular or elemental MS detection. In particular, this work will focus on integration of mass spectrometry with atomic force microscopy technologies to create and advance nanoscale multimodal physical and chemical imaging platforms. The knowledge gained from this research will contribute to the next generation of enhanced mass spectrometric analysis and characterization methods. New fundamental information and research capabilities from mass spectrometry will result that can address emerging problems relevant to many DOE missions and the general scientific community.

FY 2012 HIGHLIGHTS

We integrated ambient laser ablation using a laser microdissection instrument with atmospheric pressure chemical ionization and mass spectrometry detection. This novel combination was shown to provide multimodal imaging capability with the ability to co-register both bright field and fluorescence microscopy images of a surface and the mass spectrometry-based chemical images. The mass spectrometric detection was sufficiently sensitive to achieve a spatial resolution in the low micrometer regime (5-10 µm) in chemical profiling experiments.

Transmission geometry laser ablation directly into a formed liquid microjuntion of a continuous flow liquid microjunction surface sampling probe (LMJ-SSP) combined with mass spectrometry detection was implemented for the analysis of intractable organic and inorganic surfaces, as well as stacked materials. We showed that both insoluble polymer surfaces and inorganic materials like silver could be analyzed indicating the possibility that stacked thin film devices containing both organic and inorganic components such as polymer batteries and organic photovoltaics could be analyzed in situ.

Chemical Analysis of Complex Molecules and Small Particles

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Funding:	$730,000

PROGRAM SCOPE

Our research emphasizes basic science underlying the instrumentation and technique development that is highly relevant to DOE energy and environmental missions. We investigate physical and chemical phenomena underlying chemical analysis of complex molecules and small particles in complex environments using mass spectrometry. Specifically, our research is focused on obtaining a fundamental understanding of the activation and dissociation of complex molecular ions in mass spectrometry, understanding chemical and physical consequences of ion-surface collisions, and achieving a fundamental understanding of the properties and the chemical and physical transformations of small particles. To achieve these goals, we have developed unique instrumentation for studying physical and chemical phenomena underlying ion-surface collisions and for comprehensive physical and chemical characterization of nanoparticles. These one-of-a-kind experimental tools have been used to address a variety of analytical challenges associated with chemical analysis of molecules in complex environments and for controlled preparation of novel materials.

FY 2012 HIGHLIGHTS

Our soft-landing experiments demonstrated controlled preparation of high surface coverage samples of monodisperse ligand-capped gold clusters on surfaces. Secondary mass spectrometry indicated that the nature of the terminal functional group and surface coverage have a strong effect on charge retention by multiplying charged clusters on self-assembled monolayer surfaces. Surface-induced dissociation experiments examined the effect of the charge and the radical on the energetics, dynamics, and mechanisms of gas-phase fragmentation of complex ions. We demonstrated that even-electron ions of model peptides containing the basic arginine residue are more stable toward fragmentation than their odd-electron counterparts and examined the role of energy and entropy effects in dissociation of these systems. Furthermore, we developed a novel approach for quantitative analysis of selected classes of compounds in complex mixtures using reactive nanospray desorption electrospray ionization mass spectrometry. The new approach enabled quantification of hundreds of carbonyl compounds in complex organic mixtures.

Our studies of chemistry and microphysics of small particles provided unique insights into their mechanisms of formation, growth, and evaporation kinetics. Specifically, we demonstrated that the composition of organic particles produced through the oxidation of a-pinene by ozone and NO3 radicals is not consistent with equilibrium partitioning of the products between the gas phase and a liquid particle. Instead, the relative abundance of organic nitrates in the particles could be explained by irreversible, kinetically-controlled uptake of the nitrates on existing particles. Furthermore, we developed a new approach that offers, for the first time, the opportunity to identify particles with different shapes, separate them, and characterize their chemical and physical properties in the transition and in free-molecular regimes with high precision, in situ, and in real-time. Because particle shape is an important attribute in determining particle properties and behavior, the new approach will contribute to our understanding of the physical and chemical properties of shape-selected complex particles.

Mass Spectrometry for Operando Catalysis Research

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Funding:	$50,000

PROGRAM SCOPE

Our research is focused on the development of new mass spectrometry-based approaches for molecular level understanding of catalytic processes and for chemical analysis of biofuels. Unique capabilities offered by the atmospheric sampling techniques open up a wide range of applications relevant to many scientific fields. In particular, recently developed atmospheric pressure surface ionization techniques enable very sensitive and fast characterization of many types of compounds (polar and nonpolar, low and high molecular weight) adsorbed on substrates. Application of these techniques to catalysis research has the potential for development of uniquely versatile tools for highly-sensitive analysis of substrates at elevated pressures that will enable chemical characterization of components on catalytic substrates while the catalyst is actually operating. In addition, ambient ionization techniques are ideally suited for chemical analysis of biofuels.

FY 2012 HIGHLIGHTS

We have recently developed nanospray desorption electrospray ionization (nano-DESI), an ambient surface ionization technique that relies on the online liquid extraction of analytes from surfaces. This technique has been applied to the analysis of liquid petroleum crude oil samples as model systems for biofuels. Our results demonstrated that nano-DESI enables rapid screening of different classes of compounds in crude oil samples based on their solubility in solvents, some of which are rarely used for petroleum characterization, providing better coverage of the crude oil composition as compared to electrospray ionization. Furthermore, we developed reactive nano-DESI as a tool for examining the presence of specific functional groups and for the quantification of compounds possessing these groups in complex mixtures. These studies present first steps toward rapid quantitative analysis of biofuels using ambient surface ionization mass spectrometry.

Solar Photochemistry

Institutions Receiving Grants

Magnetic Resonance and Optical Spectroscopic Studies of Carotenoids

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Molnar, Peter, Pécs-Hungary, University of
Students: 2 Postdoctoral Fellow(s), 2 Graduate(s), 2 Undergraduate(s)
Funding: $145,000

PROGRAM SCOPE

It is our goal to study how the host lattice, in particular, affects the electron donor and charge transfer properties of carotenoids. Such information is needed before optimum use of them as antennas, photoprotectors, antioxidants and radical scavengers can be made in artificial photosynthetic systems. Carotenoids are intrinsic components of reaction centers and pigment-protein complexes in photosynthetic membranes of plants, algae, and cyanobacteria. They play a crucial photoprotective role by quenching and dissipating the excess energy, thereby dramatically prolonging photochemical energy conversion ability. Carotenoid radical cations ($Car^{\bullet+}$) have been identified to occur in photosystem II (PSII) as a result of the carotenoid acting as an intermediate electron carrier when chlorophyll (Chlz) is the electron donor to $P^{+}680$ that protects the PS II against the uncontrolled oxidative reactions of the oxidizing $P^{+}680$. This was confirmed by genetic modification and supported by EPR and by the x-ray structure of PS II. Carotenoid radical cations also serve to dissipate excess energy by the carotenoid zeaxanthin (zea) forming a heterodimer (Holt, et al., *Science*, *307*, 433 (2005)) with chlorophyll, which then undergoes charge separation in light harvesting center II (LHC II). It was recently found that lutein (Lut) is involved in another charge-transfer $Lut^{\bullet+}\cdots Chl^{\bullet-}$ quenching site besides that of Zea.

FY 2012 HIGHLIGHTS

We found that the photoprotective ability of certain carotenoids in photosynthetic systems correlates with their ability to form carotenoid neutral radical (#$Car^{\bullet}$) by proton loss from carotenoid radical cations ($Car^{\bullet+}$). The carotenoid neutral radical was identified in PSII, and we have just found evidence for it in light activated leaves. The results support our original proposal that #$Car^{\bullet}$ provides effective nonphotochemical quenching of the singlet and triplet excited state of chlorophyll (Chl), protecting the photosynthetic apparatus from damage by excess light. We found that substituent groups such as epoxy and allene interrupt electronic conjugation and destabilize the neutral radicals or even prevent their formation. We are now determining how other substituents (methoxy, hydroxy, carbonyl, keto and terminal substituted rings) alter carotenoid properties in the presence of metal ions. The development of practical devices to better utilize solar energy as a readily available source of energy will benefit from understanding how excess energy can be safely quenched.

Supramolecular Structures for Photochemical Energy Conversion

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	Moore, Thomas A., Arizona State University
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Funding:	$175,000

PROGRAM SCOPE

Fundamental aspects 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 underlying the natural photosynthetic process. Two aspects of artificial photosynthesis are under study. The first 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, and in sensors for various purposes. The second part of the study involves the roles of carotenoid polyenes in artificial photosynthesis. Carotenoids are important in photosynthesis 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.

FY 2012 HIGHLIGHTS

A new method of synthesizing porphyrin-containing electrically conductive polymers was discovered. This method allows the preparation of a polymer that is soluble in organic solvents. This is an important advance, as the polymers previously prepared in the project could only be formed on the surfaces of electrodes. Future work involves investigating the properties of this new porphyrin polymer. In conjunction with the polymer synthesis work, a new method for chemically linking porphyrins using copper salts was discovered. This method may be useful for the preparation of a variety of new materials.

Several photosynthetic model compounds consisting of phthalocyanines (relatives of chlorophyll) chemically linked to carotenoid polyenes of various structures were synthesized and studied using advanced transient spectroscopic methods with high time resolution. These studies revealed interesting, unexpected features of the transfer of excitation energy from the carotenoids to the phthalocyanines. These studies are continuing and are helping us understand aspects of natural photosynthetic antennas, which are responsible for gathering essentially all of the sunlight used in photosynthetic conversion of sunlight into useful energy stored in chemical bonds.

Electronically Wired "Semiconductor Nanoparticles: Toward Vectoral Electron Transport in Hybrid Materials"

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Students:	0 Postdoctoral Fellow(s), 4 Graduate(s), 0 Undergraduate(s)
Funding:	$225,000

PROGRAM SCOPE

We are focused on the development and characterization of new semiconductor nanorod materials interfaced to both metallic catalytic sites and unique metal oxide nanoparticles. The asymmetric arrangement of these nanomaterials is designed to ensure vectorial electron transfer in photo-electrochemical processes which may ultimately provide pathways toward the formation of chemical fuels from sunlight.

FY 2012 HIGHLIGHTS

The Armstrong/Saavedra groups have continued the exploration of the energetics of charge transfer processes to monolayer-tethered CdSe nanocrystals (NCs) on electroactive waveguide surfaces. We have explored the changes in conduction band energies that result as coverage of the CdSe NCs increases, which is important in controlling their catalytic activity in arrays of photoactive NCs. We have also used potential-modulated attenuated total reflectance (PM-ATR) spectroelectrochemistries to estimate charge injection rates into these NCs, determining that they exist at high coverages in at least two distinct sub-populations.

To extend these studies to semiconductor nanorods (NRs) and to assess the orientation of NR assemblies on semiconductor electrodes, an ATR spectrometer combined with a Langmiur-Blodgett trough was designed and built in the Saavedra group. Nanorod assemblies on electrodes have been prepared and are being characterized to probe relationships between macroscopic orientation, spectroelectrochemical and catalytic properties, and frontier orbital energies.

New efforts by Pyun have enabled the synthesis of a new class of nanostructured photocatalysts that combine, in a high modular fashion, light harvesting semiconductor nanorods, selectively decorated with HER or OER type catalytic inclusions. This work was recently published in *ACS Nano* and highlighted by the editor as an important synthetic advance in the field of nanomaterials.

Development of Earth-Abundant Transition Metal Catalysts for Water Oxidation

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Funding:	$200,000

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 dodecafluoropinacolate ($ddfp^{2-}$) 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.

FY 2012 HIGHLIGHTS

We have prepared a family of new earth-abundant transition metal compounds of the form $A_2[M(ddfp)_2]$, with A = K^+, Me_4N^+, or nBu_4N^+ and M = Fe, Co, Ni, Cu, and Zn. Compounds have been characterized by single-crystal x-ray crystallography, UV-vis spectroscopy, solution magnetic susceptibility and cyclic voltammetry. Several Lewis base adducts of the form $A_2[M(L)(ddfp)_2]$ have also been prepared. The four-coordinate compounds are rigidly square-planar except for the Zn derivatives which are distorted toward tetrahedral geometry. The five-coordinate species are square-pyramidal and only bind stronger Lewis bases such as H_2O and py, but not THF, acetone, or CH_2Cl_2. The K^+ salts are fully soluble in water, the Me_4N^+ salts have some solubility, but the nBu_4N^+ salts are only soluble in polar, aprotic solvents. Binding of water has been characterized by UV-vis spectroscopy for Co, does not occur for Cu; and current data on Ni suggest some binding, but a weaker equilibrium than with Co.

Aqueous titrations of $[Co(ddfp)_2]^{2-}$ indicate three pK_b values that are quite close, and only upon the fourth addition of H^+ does the complex fall apart. Cyclic voltammetry in H_2O exhibits an oxidation feature at 0.6 V versus the Ag/AgCl followed by a catalytic wave at 1.2 V in potassium nitrate (KNO_3) electrolyte. The same strong oxidation wave was also obtained in other electrolytes including NaF, NaOAc and NaH_2PO_4. The formation of gas bubbles was observed on the electrode surface over several scans, likely indicative of O_2 release. Support for a homogeneous catalyst includes the following. (1) No discoloration of the electrode during CV measurements occurs nor any deposition on the electrode surface takes place. (2) No catalytic wave due to water oxidation was observed using an unpolished carbon electrode from multiple CV scans cycled in a fresh cobalt-free KNO_3 electrolyte at pH 10.0. (3) The observed activity for $[Co(ddfp)_2]^{2-}$ complex is independent of electrolyte. (4) The electronic spectra of 2 in the presence of all electrolytes, except NaH_2PO_4, clearly show no difference from the spectra of 2 solely in water.

Low Power Upconversion for Solar Fuels Photochemistry

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Funding:	$178,000

PROGRAM SCOPE

The proposed research is composed of two parallel lines of inquiry addressing fundamental aspects of photo-induced energy transfer processes as they relate to the emerging topic of solar photon wavelength upconversion achieved through the regenerative photochemical process of sensitized triplet-triplet annihilation (TTA). The concepts developed in this proposal address topics and processes central to solar energy conversion while being cognizant of sustainable sensitizer design and compatibility of the proposed photochemical processes within aqueous environments. First, we seek to translate sensitized TTA-based upconversion into more sustainable formats using highly abundant elements in sensitizer design. Two representative molecular designs will be developed to promote intramolecular triplet state generation for use in upconversion schemes: (1) new Cu^{I} charge transfer sensitizers designed to possess markedly extended excited state lifetimes using pendant triplet acceptors to intramolecularly produce either “pure” organic triplets or equilibrated excited states based on the triplet reservoir effect; and (2) high extinction coefficient Sn^{IV} porphyrin sensitizers covalently tethered to energetically appropriate acceptors/annihilators in their axial positions, thereby circumventing the limitations imposed by bimolecular triplet sensitization. The second series of proposed investigations address a key criterion for potential integration into solar fuels producing schemes, namely photochemical upconversion, that decisively function in water.

FY 2012 HIGHLIGHTS

During this first month of funding, we have successfully demonstrated solution-based photon upconversion between several established and newly synthesized homoleptic Cu(I) diimine-based visible light sensitizers in conjunction with a variety of acceptor/annihilator molecules. Progress has also been made on the synthesis of a Sn^{IV} porphyrin bearing a pendant anthracene moiety in its two axial positions.

Synthesis and Characterization of WS_2 and Cu_2O as Solar Energy Conversion Materials

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Funding:	$190,000

PROGRAM SCOPE

Our goal is to study, understand, and improve upon earth-abundant semiconductors in order to determine their value as solar energy conversion materials. Tungsten disulfide and cuprous oxide are promising solar energy conversion materials as evinced by their band gaps (WS_2 - 1.35 eV; Cu_2O – 2.0 eV) and large absorption coefficients in the visible light range. However, these materials have seen limited use in solar energy conversion devices for a number of reasons. Among them, WS_2 has been limited by poor scalability of the processes used to produce it and Cu_2O has been limited by reductive instability in aqueous solution.

FY 2012 HIGHLIGHTS

We have developed a method for generating thin films of crystalline WS_2 from polysulfide flux. When such a film is synthesized from a tungsten foil by heating briefly to 800°C in the presence of sodium sulfide and excess sulfur, the excess sulfur combines with the sodium sulfide to yield liquid sodium polysulfide, which is believed to dissolve the tungsten metal and deposit the sulfide upon cooling.

In order to resolve the problem of reductive instability for Cu_2O in aqueous electrolytes, we have utilized atomic layer deposition (ALD) to generate thin films of metal oxides on the Cu_2O surface to function as a chemical diffusion barrier while still permitting electron tunneling. After several ALD cycles, Cu_2O electrodes exhibit highly resistive behavior due to the formation of an insulating surface oxide. Nevertheless, the electrodes retained high V_{OC} values, suggesting that the deposition process did not result in deleterious surface chemistry, such as surface Cu formation. Thus these experiments demonstrate the viability of ALD as a method for depositing thin oxide films on Cu_2O without undesirable surface reactions.

Membrane-Organized Chemical Photoredox Systems

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

PROGRAM SCOPE

The key photoredox process in photosynthesis is the accumulation of oxidizing equivalents on a tetranuclear manganese cluster that then liberates electrons and protons from water and forms oxygen gas. Our primary goal in this project is to characterize inorganic systems that can perform this same water-splitting chemistry. One such species is the dinuclear ruthenium complex known as the blue dimer. Starting at the Ru(III,III) oxidation state, the blue dimer is oxidized up to a putative Ru(V,V) level prior to O-O bond formation. We employ electron paramagnetic resonance spectroscopy to characterize each step in this reaction cycle to gain insight into the molecular mechanism of water oxidation.

FY 2012 HIGHLIGHTS

We have made significant inroads in the characterization of the most oxidized form of the blue dimer, Ru(V,V). Instead of two ruthenyl centers, each oxidized by five electrons, we find evidence of significant oxyl-radical character. Another finding of particular note is the role the oxidant plays in the mechanism of the reaction. Aside from removing electrons, we showed that ceric ammonium nitrate (CAN) dramatically alters the spectral properties of the blue dimer, implying non-innocent behavior that leads to wholly different intermediates compared to those generated using any of a number of other oxidants. This is of critical relevance as CAN has been the oxidant of choice for many labs studying this reaction for nearly 30 years. Thus previous mechanistic proposals for blue dimer catalyzed water oxidation may need to be re-evaluated.

Fundamental Studies of Energy- and Hole/Electron-Transfer in Hydroporphyrin Architectures

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Funding:	$165,000

PROGRAM SCOPE

The long-term objective of the Bocian/Holten/Lindsey 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 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 group), and electrochemical, electron paramagnetic resonance, and resonance Raman studies, as well as density functional theory calculations (Bocian Group).

FY 2012 HIGHLIGHTS

A number of novel bacteriochlorins have been synthesized and characterized with the aim of extending the absorption further into the near-infrared region of the spectrum. The electron/hole transfer rates have also been determined for a series of singly oxidized tetrapyrrolic arrays using a novel thallium hyperfine clocking strategy.

Nanoscaled Components for Improved Efficiency in a Multipanel Photocatalytic Water-Splitting Device

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Funding:	$125,000

PROGRAM SCOPE

We have constructed a practical photolytic system for quantum efficient production of hydrogen. Our approach is based on the assembly of a multi-component integrated system for direct photocatalytic splitting of water for the efficient production of hydrogen. We propose to produce hydrogen as an energy source that is cost-competitive with fossil fuels and without the concomitant production of greenhouse gases.

The concept is quite straightforward. In order to achieve the over potential required for direct water splitting, the device is composed of multiple dye-sensitized cells directly linked in series. The advantage of this concept is that each cell needs to contribute only a fraction of the overall potential required for water splitting, thus permitting device engineering to maximize efficiently without regard to electric potential. Progress and barriers to practical application will be described.

TiO_2 photocatalytic materials are especially attractive for their non-toxic, clean, and low-cost properties as well as their thermal stability. Usually, TiO_2 can be prepared by wet process (e.g., sol-gel), anodization, or sputtering method. As shown in some papers, the thin TiO_2 films synthesized by a wet process have shown high photocatalytic reactivity, but their mechanical durability is less stable. In our previous efforts in this field, TiO_2 films were prepared by the high-voltage anodization technique. Formation of H_2 and O_2 gas was observed using our multipanel photocatalytic water-splitting device under Xe lamp.

FY 2012 HIGHLIGHTS

We have prepared a new series of ruthenium based dye sensitizers (T1, T2, & T2) that exhibit broad absorption in the region of the solar spectrum. The preparation of these materials is straight forward and proceeds in good overall yield. The syntheses are readily amendable for the preparation of derivatives in order to fine tune absorption characteristics.

New Transition Metal Building Blocks and Assemblies for Photocatalytic Fuel Production

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Funding: $195,000

PROGRAM SCOPE

This project is directed toward addressing fundamental questions that underlie the conversion of carbon dioxide to a solar fuel via artificial photosynthesis. The research focuses on the development of new metal–alkylidyne (MCR) chromophore/sensitizers; our work has demonstrated MCR compounds possess highly reducing excited states suitable for activating carbon dioxide reduction catalysts, and proton-coupled electron-transfer chemistry that could allow them to function without conventional sacrificial donors. The project has three major objectives: (1) to understand the excited-state electron-transfer mechanisms and rates of MCR–antenna dyads, (2) to develop MCR proton-coupled electron-transfer catalytic cycles for extracting reducing equivalents from renewable resources, and (3) to synthetically integrate these components with catalysts to form MCR–antenna–catalyst assemblies and to study their photophysical and photochemical properties. The results from these three objectives will provide fundamental insights that are expected to form the basis for design rules for functional photocatalytic materials capable of producing solar fuels from carbon dioxide. The significance of the research project is that its major objectives overlay with fundamental challenges that must be solved for the development of functional solar-fuel producing assemblies, such as how to integrate photochemical, redox-catalysis, and electron-supply modules in a closed cycle to drive the activation of inert feedstocks.

FY 2012 HIGHLIGHTS

During the past year, we have completed a comprehensive experimental and theoretical study of the molecular structure of a prototypical MCR compound in its ground, oxidized, and electronically excited states. This study demonstrates that MCR compounds will undergo photochemical electron transfer reactions with small reorganization energies. We also showed that photochemical excitation of self-assembled MCR–antenna dyads results in efficient energy transfer from the antenna to the reducing MCR excited state, meeting a criterion of a functional system. During the next period, we will combine these dyads with reduction catalysts and test their photochemical reactivity with carbon dioxide.

Transition Metal Polypyridine Complexes: Studies of Mediation in Dye-Sensitized Solar Cells and Charge Separation in Molecular Assemblies

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Funding:	$165,000

PROGRAM SCOPE

The research ongoing in DE-FG02-04ER15591 comprises two parts, both of which focus on fundamental aspects of photoinduced charge separation. Each part is based on systems that are chemically dissimilar, but the fundamental underlying principles are not. Absorbed light initiates a cascade of electron transfer processes. Relative rates of electron transfer steps leading to charge separation or charge recombination define the final efficiency. Manipulation of the structural components provides the means to change and control those rates. With that control, charge separation can, in principle, be made to predominate over the energetically more favorable charge recombination.

The first part involves studies of supramolecular assemblies designed to undergo long-lived, photoinduced charge-separation. In this regard, considerable past efforts from a number of laboratories, including ours, have focused on ruthenium-based chromophores with good success. Unfortunately, ruthenium is both expensive and not earth-abundant. The current strategies focus on chromophores based on Cu(I), which is earth abundant. Fabrication of the assemblies takes advantage of the fact that Cu(I) forms labile complexes and relies on spontaneous self-assembly. The strategy further builds on the knowledge gained in our past DOE-funded studies with ruthenium-based donor-chromomophore-acceptor (D-C-A) triads—specifically, the exploitation of the ground-state D/C association to promote efficient, fast, *multi-step* charge separation. We have also determined that spin chemistry of Cu(I) chromophores (similar to ruthenium analogs) is a critical element in the photophysics of the charge separated states (CSS). We are working to develop a full understanding of this spin chemistry and how it relates to CSS formation and recombination.

The second part involves studies on dye-sensitized photoelectrochemical solar cells (DSSC) employing mediators based on cobalt polypyridine complexes. The cobalt-based mediator systems provide opportunities for systematic study of DSSCs in ways that are simply not possible with the archetypical mediator system, I^-/I_3^-. For instance, iodide is not amenable to chemical modification, while the structural, redox, and optical properties of cobalt polypyridine complexes are. In these studies, we focus on several aspects of cobalt-based mediators, including systems with highly electron deficient ligands that present the prospect of substantially increasing open-circuit voltage, V_{oc} and copper-based dyes which are stable in contact with cobalt mediators, but not I_3^-.

Applications to Adaptive Quantum Control to Research Questions in Solar Energy Conversion

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Funding:	$170,000

PROGRAM SCOPE

This renewal proposal explores several photoactive systems at the heart of third generation solar energy conversion strategies, using advanced coherent control spectroscopies such as adaptive pulse shaping. In one area of research, we consider new tunable bichromophoric molecules supporting singlet fission to understand the role of specific nuclear motions and electronic coupling pathways for altering photoreactivity and mechanism. With such systems we will 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.

Singlet Fission

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Funding:	$150,000

PROGRAM SCOPE

We propose to combine experimental and theoretical tools to improve the presently unsatisfactory understanding of the singlet fission (SF) process to a level that will allow efficient design of (1) new SF chromophores with optimal excitation energies, ~2.2 eV for S_1, and ~1.1 eV for T_1; and (2) optimal modes of inter-chromophore coupling. Our goal is the development of a predictive competence for the design of useful materials for 200% triplet yield from SF in a dimer, oligomer, aggregate, polymer, or solid. In addition, we propose to examine the possibility that the Jablonski diagram could be expanded by observation and study of excited quintet states of π-electron systems with closed-shell ground states. 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.

Study of Multiple Exciton Generation with New Multi-Dimensional Spectroscopies

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Funding:	$200,000

PROGRAM SCOPE

The goal of the project is to probe, identify, and understand the physical mechanisms required for more efficient third-generation photovoltaics based on carrier multiplication. In bulk semiconductors, light directly excites one electron-hole pair per incident photon. The efficiency of existing solar cells is limited by losses due to rapid cooling of electrons excited above the band gap. In quantum dots, predictions of slower cooling, increased coupling between excitons, and relaxation of bulk selection rules led to suggestions that generation of multiple electron-hole pairs per incident photon might be exploited to improve the efficiency of photovoltaics and solar fuel generation. The project is aimed at developing and spreading new optical measurements that will accurately determine the yield, reveal the mechanism of multiple electron-hole pair generation, and uncover the factors that control the yield in semiconductor nanocrystals. Proposed theories of multiple electron-hole pair generation have crucial differences in the dephasing mechanism and the magnitude of the Coulombic couplings. In quantum dots, the project measures the dynamics of "hot" states with energies near the electron-hole pair multiplication threshold and directly characterizes multiple exciton states via measurements of Auger recombination (the reverse process of carrier multiplication) and femtosecond 2D spectroscopy, a technique capable of measuring both the coupling and dephasing involved in the mechanism. This requires extending 2D spectroscopy into the short-wave infrared (1-2 micron wavelength) where the bandgap of efficient third-generation photovoltaics must lie.

FY 2012 HIGHLIGHTS

Measurements of Auger recombination out to 1 ns delay for absolutely calibrated excitation probabilities of up to 10 suggest charging. For less than 1 electron-hole pair per dot, the data are consistent with accumulated charging models, with a product of charged state quantum yield and lifetime in the range 10-50 ms. However, for excitation probabilities above 2, the data are quantitatively inconsistent with accumulated charging models. To enable studies of Auger recombination without accumulated charging, we have built a new beam scanning apparatus.

We have constructed a novel femtosecond 2D spectrometer that covers the entire short-wave infrared and supports pulse durations as short as 10 fs. The wide bandwidth is achieved by a Brewster angle interferometer. We have preliminary 2D spectra of low bandgap quantum dots and are working to improve the signal-to-noise ratio.

Graphene Charge Transfer, Spectroscopy, and Photochemical Reactions

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Funding:	$200,000

PROGRAM SCOPE

This project focuses on the special electronic and optical properties of graphene and 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 Qdots 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 are working on several basic science experiments related to these goals.

FY 2012 HIGHLIGHTS

We have explored the question of possible surface enhanced Raman spectroscopy (SERS) from charge transfer by adsorbed molecules onto graphene substrates. In order to carefully investigate the question of possible chemical SERS, we studied Rhodamine 6G dye (R6G) on graphene, as R6G is the standard, well characterized molecule for high Raman cross section SERS with Ag particles. By comparing the optical contrast visible spectrum, and the Raman spectrum, we were able to determine the absolute Raman cross section for R6G on the graphene surface. We find that the R6G section is perhaps a factor of 3 less on the graphene surface, apparently because the R6G absorption is red-shifted away from the laser line. In this system, there is no evidence for field enhancement or chemical SERS. Nevertheless, the R6G Raman shows high signal to noise, as interfering dye luminescence, present for example for R6G in solution, is strongly quenched by the metallic graphene. In addition, luminescence from the graphene itself is negligible despite 2% optical absorption of the laser. As a net result, graphene makes an excellent substrate for Raman scattering by adsorbed molecular species.

Theoretical Studies of Photoactive Molecular Systems: Electron Transfer, Energy Transport, and Optical Spectroscopy

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

PROGRAM SCOPE

This program is focused on the development of theoretical methods for addressing problems of importance to the DOE Solar Photochemistry program, and applying these methods to specific systems of interest in solar energy conversion. The methods development is focused on first principles quantum chemical approaches, particularly density functional theory (DFT). We are developing a novel methodology using localized orbital corrections (LOCs) which is capable of yielding quantitatively accurate results for various thermochemical properties, including reaction energies, redox potentials, spin splittings, and solvation free energies. Recent developments have addressed transition metal containing systems which have historically posed severe challenges for quantum chemical calculations. Accuracies of ~2-3 kcal/mole for these systems, as opposed to the ~10 kcal/mole obtained using standard DFT functionals such as B3LYP, have been achieved. Specific solar energy conversion systems to be studied include the Gratzel cell (TiO_2 nanoparticles in solution) and transition metal based water splitting complexes. Our initial objectives are to provide a detailed, atomic level description of the electron trapping and transport, and (in the case of water splitting) key chemical reactions in these systems. Ultimately, our methods are intended to contribute to the design of improved energy conversion systems.

FY 2012 HIGHLIGHTS

We focus here on two major accomplishments of FY 2012. The first is extension of our DFT-LOC methodology to the calculation of redox potentials for transition metal containing systems. We extracted more than 100 transition metal complexes with experimental redox potentials from the literature, and compared the results of our new approach to those obtained with standard B3LYP calculations. We were able to reduce the average error in the redox potential computations from ~0.4 eV to ~0.1 eV, with the latter value being close to experimental error. The second major accomplishment is the first realistic modeling of TiO_2 nanoparticles in solution in which extensive comparison with experimental data demonstrates the quantitative validity of the quantum chemical calculations. We computed quantities such as the open circuit voltage and conduction band shift of the system, achieving agreement with experiment within ~0.1eV. The application of the redox potential corrections discussed previously were necessary to obtain this level of agreement. Finally, we have investigated the ambipolar model for carrier diffusion in this system proposed by a number of experimental groups (in which electrons travel through the material in concert with small ions, typically Li^+ in working Gratzel cells) and identified trapping states consistent with this model, at an appropriate energy below the conduction band. The barrier for transition between two neighboring states (involving coupled electron-ion motion) is also consistent with experimental measurement of the temperature dependence of charge transport.

Organic, Nanoscale, and Self-Assembled Structures Relevant to Solar Energy Conversion

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Funding:	$180,000

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.

FY 2012 HIGHLIGHTS

Towards this goal, this program focuses on (1) delineating new compositions of matter relevant to solar energy conversion; (2) understanding the basic photophysical properties of next-generation conjugated materials for excitonic solar cells; (3) 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; (4) probing the extent of electronic coupling between conjugated organic materials and nanoscale structures in both ground and excited states; and (5) 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.

Colloidal Type II Nanorod Based Triad/Antenna Complexes for Solar-Fuel Conversion

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Funding:	$162,648

PROGRAM SCOPE

The long-term goal of this project is to prepare and investigate colloidal semiconductor nanostructure assemblies consisting of light harvesting antenna and charge separation triads that are capable of efficient photon absorption, charge separation, and accumulation, as well as catalysis under solar flux. Mimicking molecular triads, the proposed inorganic triads are based on epitaxially grown type II hetero-nanorods (NR) with attached catalyst (such as CdSe-CdS-Pt), which have built-in directional charge separation and catalysis units as well as tunable optical and electronic properties (by varying the materials, their dimensions, and the extent of quantum confinement). The antenna system consists of quantum dots or molecular chromophores, which enhances light harvesting rate by energy transfer to the triad and/or by plasmonic field enhancement. The design and improvement of such photocatalytic antenna/triad complexes requires a fundamental understanding of the photophysics and charge transfer properties of triads, as well as energy transfer dynamics between the antenna and the triads and the effect of plasmonic fields on the exciton dynamics (relaxation, transfer, and dissociation). Therefore, a fundamental study of these processes in model triad/antenna complexes is the focus of the proposed research plan. The specific objectives are to (1) investigate single and multiple exciton relaxation as well as single and multiple charge separation and recombination dynamics in NR-based dyads (type II NRs) and triads (type II NRs + catalysts) by transient absorption (TA) spectroscopy, and (2) investigate the factors controlling the energy transfer efficiencies between the light harvesting antenna and nanorod triads using both ensemble averaged and single complex/spatially resolved spectroscopy.

FY 2012 HIGHLIGHTS

The grant started on September 15, 2012. During the required report period (September 15 to September 30, 2012), we have succeeded in the preparation of CdSe-CdS-Pt triadic nanorods. Ongoing studies are characterizing the charge separation dynamics and their dependence on the dimension of the CdSe dot and CdS rod.

Solar Energy-Driven Multi-Electron-Transfer Catalysts for Water Splitting: Robust and Carbon-Free Nano-Triads

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Funding: $300,000

PROGRAM SCOPE

The overall thrust is to conduct fundamental research on the success limiting factors in realizing more efficient and stable visible-light-driven water oxidation/splitting systems. We are using closely integrated experimental and computational approaches and targeting the synthetic, photophysical and photochemical properties of photo-driven water oxidation dyads and triads. The specific objectives of this multi-disciplinary research project are: (1) to prepare and characterize strongly associated semiconductor metal oxide (SMO)-$[Ru^{II}(bpy')_3]$-polyoxometalate water oxidation catalyst (POM WOC) triads using zwitterionic linking $[Ru(bpy')_3]$ sensitizers; (2) to prepare and characterize single unit (molecular) sensitizer-POM WOC dyads and use these to make triads with an SMO; (3) to prepare and characterize tunable colored SMO-POM WOC dyads, where the colored SMOs will function as the light-harvesting component in order to overcome the potential instability of organic containing sensitizers; (4) to prepare and characterize all-inorganic SMO-M-WOC triads [M=Ce, Cr, Co], the chromophores of which are d-electron-metal-ion-to-nanoparticle charge transfer complexes; (5) to develop extremely fast, selective and stable water oxidation catalysts (WOCs) as this remains a bottleneck in solar fuel production assemblies; and (6) to develop computational approaches for the study of interfacial electron transfer dynamics in the proposed dyads and triads.

FY 2012 HIGHLIGHTS

Our team has realized progress on all six of the above goals but we highlight the following achievements. (1) We prepared and characterized (SMO)-$[Ru^{II}(bpy')_3]$-WOC triads, measured their dynamic properties, and documented very fast electron transfer from the bound WOC to the photogenerated Ru(bpy)$_3$-based triad hole. (2) We investigated the electron and hole spectral signature and dynamics of α-Fe_2O_3 photoanodes under water oxidation conditions. (3) We prepared two new classes of extremely robust complexes that exhibit intense but short-lived metal-to-polyoxometalate charge transfer transitions in the visible. (4) We designed and prepared two new types of POM WOCs, one of which is the fastest reported to date (>4000 s^{-1}; the OEC turns over at 150-400 s^{-1}) and absolutely molecular under our operation conditions (not simply a precursor for a metal oxide particle WOC based on many independent experiments), (5) We elucidated the nature of the TiO_2 surfaces, as well as the structure of a functionalized chromophores, L*CH, on the TiO_2 surfaces, i.e., L*CH@TiO_2, in the liquid water. (6) We developed and validated fastest and optimal computational approaches, such as the self-consistent charge density functional tight-binding (SCC-DFTB) and transition-charge-density-model, to study electron transfer dynamics in the L*CH@TiO_2 systems.

Conjugated Polymers and Polyelectrolytes in Solar Photoconversion

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Students:	2 Postdoctoral Fellow(s), 3 Graduate(s), 0 Undergraduate(s)
Funding:	$350,000

PROGRAM SCOPE

Conjugated polyelectrolytes (CPEs) combine a π-conjugated backbone with polyelectrolyte character imparted by substitution of the arylene repeat units with ionic solubilizing groups. This research program is investigating the fundamental properties of conjugated polyelectrolytes, with emphasis placed on studies of excited state energy transport, self-assembly into CPE-based films and colloids, and exciton transport and charge injection in CPE films constructed atop wide bandgap semiconductors. In the most recent progress period, we have also extended efforts to examine the properties of low-bandgap donor-acceptor conjugated polyelectrolytes that feature strong visible light absorption and the ability to adsorb to metal-oxide interfaces. Over the past year, this program has had several specific objectives, including (1) the design, synthesis, and characterization of structurally well-defined conjugated polyelectrolyte structures, including conjugated polyelectrolyte dendrimers (CPDs) and conjugated polyelectrolyte oligomers (CPOs); (2) the investigation of the photophysical properties of CPD and CPO structures using steady state and ultrafast time-resolved spectroscopy; (3) the design, synthesis, and photophysical characterization of electron donor-acceptor ion-containing conjugated oligomer and polymer systems; and (4) the study the physical and photoelectrochemical properties of CPE films adsorbed on crystalline and nanostructured TiO_2 interfaces.

FY 2012 HIGHLIGHTS

The synthesis and complete photophysical characterization of several series of conjugated polyelectrolyte dendrimers and oligomers have been accomplished. The photophysical results show that the “amplified fluorescence quenching” effect occurs in these systems. Remarkably the Stern-Volmer fluorescence quenching efficiencies for 3rd generation dendrimers and the longest oligomer (9 repeat units) approaches that seen for high molecular weight polymers with similar conjugated structure. In parallel efforts, the photophysical characterization of two distinct series of donor-acceptor oligomer structures that feature ionic pendant groups has been accomplished. These donor-acceptor oligomers absorb broadly throughout the visible and near-infrared regions, and they adsorb strongly onto TiO_2 surfaces from solution. Photoelectrochemical study of the oligomer-TiO_2 films reveals interesting relationships between the electronic structure of the donor-acceptor oligomers and the efficiency by which they charge inject into TiO_2 following optical excitation.

Further Studies on Photocatalytic Water Decomposition

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Funding:	$170,000

PROGRAM SCOPE

In this project, we are using a strongly synthesis-driven approach to develop and study new and improved photocatalysts for water decomposition. A successful photocatalyst will use the energy inherent in its excited state to carry out the bond breaking and bond making steps required for the conversion of water into its elements. Efforts center around a recently discovered family of mononuclear and dinuclear Ru-based catalysts which are effective in the chemical oxidation of water to form dioxygen. At first it was presumed that the dinuclear systems created the critical O-O bond through the interaction of two proximal Ru-O centers. With the discovery of mononuclear catalysts that react by a first order pathway, more attention has been given to a mechanism involving the attack of H2O on a Ru=O species. Systematic synthetic variation of the polypyridine ligands surrounding the metal center is helping to optimize catalyst performance. We plan to recover and analyze a still-active catalyst as a probe of mechanism, and we will immobilize a catalyst on a surface such as TiO2 and analyze reactivity. We are looking carefully at the dinuclear catalysts developed in the previous cycle of funding to determine the possible advantage of multiple metal centers in managing access to higher oxidation states. Together with Etsuko Fujita at Brookhaven we are investigating bidentate and tridentate ligands containing the 4-azaacridine moiety wherein the uncomplexed nitrogen on the central ring can mediate proton transfer and, ultimately, the photoreduction of protons through an NADH-type intermediate.

FY 2012 HIGHLIGHTS

Using simple LED lights as the irradiation source, we have succeeded in the photoactivation of our mono- and dinuclear Ru(II) water oxidation catalysts. Although the strong oxidant Ce(IV) is no longer necessary, our system still requires a good electron acceptor such as sodium persulfate. Careful control of pH through buffering of the solution is also necessary. Furthermore, using an appropriate bridging ligand, we have incorporated both the photosensitizer and the oxidation catalyst into a singular molecular assembly and demonstrated that this dyad assembly functions more efficiently than the corresponding bimolecular system. We are now beginning to examine water reduction in hopes of replacing the sacrificial electron acceptor, leading to a truly catalytic water splitting system.

Physical Chemistry of Reaction Dynamics in Ionic Liquids

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Funding:	$164,000

PROGRAM SCOPE

Our BES-funded research is part of a small collaborative project between the groups of Blank, Castner, Margulis, Maroncelli, and Wishart that focuses on experimental and theoretical studies of photo-initiated electron transfer processes in novel liquids composed solely of ions. In particular, the Margulis group is interested in developing an understanding of novel room-temperature ionic-liquids from a theoretical and computational perspective. Our focus during this period has been in understanding ionic charge transport as well as excess electron localization and spectroscopy. In order to better rationalize different dynamical aspects of these systems, we have also investigated several aspects of the x-ray scattering of ionic liquids. Along these lines, we have developed methodology to partition the computationally-derived x-ray scattering structure function into components that allow us to better interpret polarity alternation, charge alternation, and other adjacency correlations that are ubiquitous in these systems. Our theoretical and computational studies make close contact with the very recent experimental findings by Blank on the ultrafast dynamics of excess electrons, and they also explain the x-ray results obtained in the Castner group. Our most recent work and work we plan to do in the near future involve close interaction with the Maroncelli group on translational and rotational diffusion of neutral and charged species. This is important to better understand processes such as bimolecular electron transfer. We also plan to tackle the problem of excess electron dynamics on the femtosecond and picosecond time scales.

FY 2012 HIGHLIGHTS

We have developed an understanding and published work on the specific pattern of localization of excess electrons in a series of different room-temperature ionic liquids. We have also been able to rationalize the spectroscopy of excess electrons and excess holes at time zero after photo-excitation. We have also focused on the mechanism of charge transport of ions in these systems and found that ion pairing concepts that are common in the ionic solution literature are perhaps less clear in binary systems solely composed of ions. Significant progress was also made in understanding the nanoscopic structure of ionic liquids. We have been able to explain that the two most significant length scales present in ionic liquids (the short length scale on which charge alternation manifests and the long length scale on which polarity alternation occurs) are both characterized by a set of positive going and negative going partial contributions that often result in significant cancellations to the overall x-ray scattering structure function.

Electron Transfer Dynamics in Efficient Molecular Solar Cells

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Funding:	$145,000

PROGRAM SCOPE

A key objective of our Department of Energy supported research is to provide kinetic models for surface mediated photochemical processes relevant to solar energy conversion. Our emphasis has been on metal-to-ligand charge-transfer (MLCT) excited states and, more recently, on singlet excited states of porphyrinic macrocycles. We have quantified the behavior of these excited states in fluid solution and at nanocrystalline (anatase) TiO_2 and insulating ZrO_2 interfaces. An important aspect of our research is to use these excited states to drive electron transfer reactions that may ultimately yield electrical power or chemical fuels.

FY 2012 HIGHLIGHTS

A series of Ru-tris(diimine) compounds have been prepared to further characterize excited state electron transfer in acetonitrile. The compounds prepared allowed the free-energy change for electron transfer (ΔG^o) to be systematically varied over a 400 meV range. A strong driving force dependence was apparent with diffusion limited rate constants for exergonic reactions and values on the order of 10^9 M^{-1} s^{-1} for $\Delta G^o \geq 0$ eV. The temperature dependence was also quantified. After corrections were made for diffusion, analysis of the activated rate constants with Marcus theory provided insights into the factors that underlie the rapid electron transfer measured for endergonic reactions. This finding indicates that iodine atoms cannot be ruled out as intermediates in the regeneration step in dye sensitized solar cells based upon thermodynamic arguments alone.

In unpublished work, we have continued studies of iodide oxidation in low dielectric constant solvents where ion-pairing is expected and is clearly evident. One particularly rewarding study still in preliminary stages involves the photo-oxidation of iodide by $Ru(deebq)(bpy)_2^{2+}$, where deebq is 4,4'-$(CO_2Et)_2$-2,2'-biquinoline, in tetrahydrofuran solution. Pulsed laser excitation resulted in the immediate appearance of $I_2^{\bullet-}$ and $Ru(deebq^-)(bpy)_2^+$ under conditions where control experiments showed that the $I^- + I^\bullet \rightarrow I_2^{\bullet-}$ reaction was much slower. This preliminary data suggests that I-I bond formation and electron transfer can occur in one concerted step from a molecular excited state. Electrochemical studies designed to identify conditions where concerted I-I bond formation might be initiated by an oxidized compound anchored to a metal oxide surface are also underway.

Hangman Catalysts for Photo- and Photoelectro- Chemical Activation of Water

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Funding:	$240,000

PROGRAM SCOPE

Light from the sun can be used as the energy input to rearrange the O–H bonds of water to the H–H and O–O bonds of hydrogen and oxygen, respectively. Of course, this cannot be accomplished directly with solar light. Catalysts and new reaction processes must be developed that will enable this bond rearrangement of water. Work in this program explores several aspects of this energy conversion process, including the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) of water splitting, the complementary fuel cell reaction, and the oxygen reduction reaction (ORR). A new class of catalysts—called Hangman catalysts—are explored with an eye towards the OER, HER and ORR conversions.

First-Row Transition Metal-Based Chromophores for Dye-Sensitized Solar Cells: Fundamental Issues and Applications

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Funding:	$190,000

PROGRAM SCOPE

The goal of the proposed research program continues to focus on the development of chromophores based on first-row transition metal ions for use in dye-sensitized, nanoparticle-based solar cells (DSSCs). The underlying motivation for our efforts concerns the question of scalability and the potential for widespread use of DSSC-based technologies. With the notable exception of the recent report of a Zn porphyrin-based sensitizer, the vast majority of research on DSSCs has focused on chromophores based on Ru(II). While such compounds are exceedingly important in terms of their historical significance with regard to the creation, characterization, and development of DSSCs over the past two decades, the elemental scarcity of Ru presents a significant obstacle to the eventual implementation of associated technologies on a global scale.

The work falls into four main categories. First, our exciting discovery of the first emissive Fe(II) polypyridyl complex has presented us with the previously unimaginable possibility of synthesizing an Fe(II) chromophore with a broad absorption cross-section in the visible having a charge-transfer state as its lowest energy excited state: in effect, an Fe(II) complex that possesses photophysical properties analogous to $[Ru(bpy)_3]^{2+}$. An extensive series of synthetic modifications to this system along with detailed spectroscopic studies are being pursued that we believe will allow us to realize this goal.

Second, we are continuing our efforts to identify (and ultimately exploit) the reaction coordinate(s) coupled to charge transfer-state deactivation through a series of studies based on the notion of torsional coordinates coupling to ultrafast surface crossing dynamics. The synthesis and characterization of several new chromophore designs are underway, in particular, a heterotrimetallic system that we believe may allow for reductive quenching of Fe(II) poypyridyl-based MLCT state(s) in order to create a more potent reductant for interfacial electron transfer into TiO_2.

Third, the compounds that are developed as part of the first two efforts are being synthetically modified in order to make them suitable for binding to nanoparticulate semiconductors. Linker strategies based on carboxylates, acetylacetonate, and hydroximates are being pursued that will allow us to fabricate stable dye-sensitized solar cells based on Fe(II) chromophores. This synthetic work will be followed by an extensive series of measurements designed to characterize the electron transfer dynamics of these sensitizers as well as demonstrate the efficacy of these compositional motifs to facilitate the creation of charge carriers. These experiments are being supported by calculations designed, in part, to examine the wavelength dependence of interfacial electron transfer from Fe(II) chromophores.

Finally, we are advancing a program for the development of chromophores involving other first-row metals, including but not exclusive to Cu(I)-based sensitizers through the synthesis, physical, and photophysical characterization of new chromophores as well as studies of interfacial electron transfer dynamics of functional Cu(I)-based DSSCs.

Molecular and Material Approaches to Overcome Kinetic and Energetic Constraints in Dye-Sensitized Solar Cells

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Funding:	$160,000

PROGRAM SCOPE

The general goal of this project is to examine changing multiple dye-sensitized solar cell (DSSC) components – redox shuttle, photoanode, sensitizer, and solvent – in concert to overcome the kinetic and energetic constraints of current generation DSSCs. A series of systematic investigations of the key kinetic processes involving each component will be performed in order to develop general structure/function relationships. For example, we intend to learn what properties of a redox shuttle will allow efficient dye regeneration with minimal driving force and recombination losses. Another question we are addressing is how the properties of photoanode material, such as surface state density, conduction band energy, and electron mobility, affect the recombination kinetics. Our longer term goal will be to use the knowledge gained from this project to guide the design of next generation DSSCs.

FY 2012 HIGHLIGHTS

The conduction band edge, Ecb, is arguably the most important physical property of the photoanode that determines the injection efficiency and electron lifetime. We developed a new method to measure Ecb for NP metal oxide electrodes: temperature-dependent spectroelectrochemical measurements of conduction band electrons. In the next period, we will extend these measurements to other materials which will allow us to understand the behavior of alternative materials in DSSCs. We have also made progress in investigating new redox shuttles. We synthesized several new cobalt complex redox shuttles to complement the cobalt polypyridyl complexes we have already been investigating. Work is in progress to understand how dye regeneration and recombination are affected as a function of ligand field. We have also made progress on understanding the effect of changing solvent systems. Initial results consisted of comparing the typically employed acetonitrile solvent with methanol to increase solubility of certain charged redox shuttles. We found that there is a dramatic effect on the energetics of each of the components (photoanode, sensitizer, redox shuttle); work is in progress to finish characterizing the changes due to solvent property and devise strategies to exploit them.

Light-Stimulated Hole Injection at Dye-Sensitized Phosphide Photocathodes

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Funding:	$140,000

PROGRAM SCOPE

The primary goal 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 photoelectrodes for solar energy storage and conversion using phosphide semiconductors. This work combines a strong experimental thrust that is guided by quantitative models of charge transfer processes. This work has two specific and interrelated research objectives. First, we are investigating hole injection processes between adsorbed photoexcited chromophores and p-type single-crystalline semiconductor electrodes to identify and elucidate the relevant kinetic, chemical, and electrochemical properties necessary for sensitized hole injection with high internal quantum efficiencies and large photovoltages. This information will be used to identify potent p-type semiconductor-chromophore-mediator combinations. Second, we are elucidating and defining the requisite design features in high (>100) aspect ratio photoelectrode architectures that (1) reduce the constraints on dye loading and dye absorption bandwidth, (2) widen the choice of compatible redox mediators, and (3) minimize the susceptibility of the adsorbed sensitizer to photodegradation without wasteful filtering of UV light. These collective features will be used to design sensitized photoelectrode architectures with high external quantum efficiencies.

FY 2012 HIGHLIGHTS

We have completed a comprehensive modeling effort that describes the operation of a sensitized photoelectrode operating under strong depletion conditions. We developed a finite difference model to account for the interplay between the bulk optoelectronic properties within a semiconductor photoelectrode and the charge-transfer kinetics at the interface with a photoexcited adlayer. We have specifically used this model to identify sensitized planar p-GaP photoelectrodes as a controllable test system for understanding and developing dye-sensitized photocathodes. In the next phase, we will demonstrate sensitized hole injection from adsorbed quantum dots into p-GaP and show the effect of covalent attachment of chromophores on the measurable quantum yields under steady-state conditions both on planar and high aspect ratio platforms.

Molecular Design of Zinc Oxide Nanocrystal-Dye Dyads and Triads

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Funding:	$295,000

PROGRAM SCOPE

We are investigating the fundamental energy and charge transfer dynamics that govern light absorption and charge separation in zinc oxide-based dye-sensitized solar cells (DSSCs). The overarching goal of this research is to study the relationship between structure, energetics, and dynamics in a set of synthetically controlled donor-acceptor dyads and triads. These studies provide access to an unprecedented understanding of the light absorption and charge transfer steps that lie at the heart of DSSCs, thus enabling significant future advances in cell efficiencies. Our work focuses on overcoming the problems associated with film heterogeneity through the use of dispersible sensitizer/ZnO nanocrystal (NC) ensembles. Well-defined molecule-like systems eliminate the heterogeneity that has plagued many prior investigations, including problems stemming from electronic communication between multiple sensitizer molecules. Monodispersed ZnO NCs in the quantum-confined regime (< 6 nm in diameter), prepared by new as well as by published methods, are used as a dispersible platform to which a variety of new sensitizers will be attached for study using ultrafast spectroscopic techniques.

FY 2012 HIGHLIGHTS

Three sensitizer/nanocrystal systems are being examined: $\mathrm{Ru[bpy(NR_2)_2]_2(dcbpy)]^{2+}}$/ZnO nanocrystal dyads, Zn(porphyrin)/ZnO nanocrystal dyads, and terthiophene/CdS nanocrystal dyads. With the first series of dyads, new ruthenium bipyridyl derivatives were synthesized by incorporating strong electron donating dialkylamino substituents, which rendered the excited state more reducing by up to 500 mV. Pump probe experiments showed the formation of an interface-bound, charge-separated pair within 100 fs that decayed within 5 ps to the long-lived oxidized dye and reduced nanocrystal. In the second dyad, the substituents on the zinc porphyrin were varied from a strong electron withdrawing cyanophenyl group to a strong electron donating (ditolylamino)phenyl substituent. The changes in both the electronic structure and excited state energy of the dyes caused measurable changes in the rate of charge injection into the ZnO nanocrystals. We are in the process of using pump-probe experiments to quantify the rate of injection. In the terthiophene/CdS nanocrystal dyads, fast electron transfer is observed using pump-probe methods when the ratio of dye to nanocrystal is near unity. As this ratio approaches 20:1, a faster excited state decay mechanism, concentration quenching, dominates. Studies of the effect of nanocrystal diameter are in progress.

Finally, new molecular dyads are being synthesized using cationic iridium(III) bipyridine and phenylpyridine complexes. Terthiophenes have been added to serve as secondary electron donors.

Physical Chemistry of Reaction Dynamics in Ionic Liquids

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Funding:	$165,000

PROGRAM SCOPE

Our BES funded research is part of a small collaborative project between the groups of Blank, Castner, Margulis, Maroncelli, and Wishart that focuses on experimental and theoretical studies of photo-initiated electron transfer processes in novel liquids composed solely of ions. In particular, the Blank group is focused on using time resolved spectroscopy and finite field simulations to investigate the dynamics and reactivity of electrons and holes following photoionization in ionic liquids. One of our primary experimental methods applies transient absorption to measure the dynamics over many orders of magnitude in time, from tens of femtoseconds to nanoseconds. Our experiments probing the absorption spectrum of the electrons and holes immediately after photoionization provide experimental benchmarks for testing the calculations by Margulis and coworkers. Our work measuring electron cooling and reactivity on ultrafast time scales is complementary to the radiolysis studies of Wishart and coworkers. Photoionization and transient absorption give accesses to a lower energy range of ionization and extend the measurements of electron and hole dynamics to shorter time scales than are accessible using radiolysis.

FY 2012 HIGHLIGHTS

We have investigated the photoionization of aliphatic ionic liquids and published work on the electron spectrum and reactivity. In this work, we demonstrated that unwanted secondary reactions products rapidly build up in the liquids during photolysis experiments. By designing and implementing a small volume watertight closed flow system, these interfering signals were avoided. The results were the first reliable measurements of the electrons and holes in ionic liquids following ultraviolet ionization with ultrafast time resolution. We successfully measured the bimodal absorption spectra of the electron and the hole prior to solvent reorganization (the dry electron), demonstrating very good agreement with the calculations by Margulis and coworkers. At delay times longer than 15 picoseconds, the evolution of the spectra qualitatively agreed with the radiolysis experiments by Wishart; however, there were important quantitative differences that reflected the lower initial energy of the photolytically generated electrons. We measured previously unobserved reactivity of the electron on a 300 fs time scale, which accounted for a significant fraction of overall electron capture. The kinetics of this ultrafast reactivity were found to be independent of electron scavenger concentration. These unusual reaction dynamics are the result of strong coupling between solvation of the electron and the reactivity of the electron. Our experiments established extension of the correlation between electron trapping and reactivity to sub-picosecond time scales.

Model Dyes for the Study of Molecule/Metal Oxide Semiconductor Interfaces and Electron Transfer Processes

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Funding: $180,000

PROGRAM SCOPE

The main objective of this research program is to engineer the interface between organic chromophores and nanostructured metal oxide semiconductors (TiO_2 and ZnO) so as to control photoinduced heterogeneous charge transfer processes through the design, synthesis, and photophysical study of organic and inorganic chromophore-spacer-anchor model compounds.

We will address heterogeneous charge transfer mechanisms which remain poorly understood, and that are important for solar energy research, through a collaborative effort encompassing a combination of molecular design, surface science, computations, and photophysical studies. Specifically, we will develop model compounds to study the following (1) the correlation between open circuit photovoltages V_{oc} and charge transfer reactions, (2) the influence of a tunable dipole built in the spacer unit on the energy level alignment of the chromophore, and (3) the mechanisms of iodide oxidation including recombination of injected electrons with oxidized iodide species. We will also address in our collaboration with the Meyer group a Stark effect recently observed with N3-rigid-rod model compounds.

Physical Chemistry of Reaction Dynamics in Ionic Liquids

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Funding: $250,000

PROGRAM SCOPE

The DOE Solar Photochemistry program is a small group grant to investigate the physical chemistry aspects of light-induced charge separation in ionic liquid solutions. The co-P.I.s are Blank (Minnesota), Castner (Rutgers), Margulis (Iowa), Maroncelli (Penn State), and Wishart (Brookhaven). Interest in using ionic liquids for energy-related applications continues to grow, as ionic liquids will become crucial parts of energy storage and conversion technologies such as batteries, fuel cells, and electrochemical supercapacitors. For this reason, it is necessary to understand exactly how the use of ionic liquids as solvents will affect the energetics and dynamics of photo-physical and -chemical processes.

Our multi-group experimental and theoretical effort will characterize excess electron solvation processes in ILs on femtosecond and picosecond time scales. Bulk structural studies will be extended to include the study of specific solvation effects of electroactive species in IL solutions; both 2D-NMR and anomalous x-ray scattering will be used to probe the interactions of IL cations and anions in contact with the redox-active solutes.

FY 2012 HIGHLIGHTS

During the FY 2012 period, the Castner research group at Rutgers both expanded previous research projects and broke ground in new research areas. Ongoing work explores reaction rates and mechanisms for both intra- and bi-molecular electron-transfer reactions in ionic liquid solutions. We continue to create reactive ionic liquids, where the anions serve as strong reductants. New work explores using cyano-substituted anions as donors.

Several articles were published on the bulk structure of ionic liquids, combining experimental work using synchrotron-based x-ray scattering experiments at the Advanced Photon Source with theoretical modeling of these experiments by the Margulis group at the University of Iowa. We study the bulk structure of the ionic liquids to determine how changing functional groups on the ions affects the short- to intermediate-range order of these fluids. New approaches include using 2D-NMR methods based on the nuclear Overhauser effect to investigate specific interactions between solute molecules and the solvent cations and anions. This has provided us with preliminary evidence that ionic liquids having long-chain substituents can create local hydrophobic regions with very different electrostatic environments.

Ground and Excited State Structures of Sensitizer Dyes Adsorbed on Semiconductor Nanoparticles

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PROGRAM SCOPE

Knowledge of the relation between the geometry and electron injection efficiency of functionalized semiconductor surfaces is of crucial importance for the design of molecular materials used in light capture. In photovoltaic cells, sensitizer dye molecules are adsorbed on a semiconductor surface, which is typically composed of the anatase phase of titanium dioxide. Crystalline phases of polyoxotitanate nanoclusters reproduce the surface characteristics of the anatase phase and, because of their well-defined periodicity, allow detailed x-ray diffraction determination of the geometry of the chromophore-nanocluster binding. The resulting information can subsequently be analyzed by theoretical calculation of the band structure and electron injection dynamics, which in turn can be related to experimental measurement of electron injection by EPR and terahertz spectroscopy. In a second stage of the project, ultrafast time-resolved pump-probe diffraction methods performed at synchrotron sources are to be used in the determination of the geometry changes of both the chromophore and the substrate on light initiated electron injection. The aim is to achieve a detailed understanding of the photo-induced electron-injection and recombination processes that take place on molecule-coated semiconductor surfaces. Different anchoring modes will be analyzed in order to allow design optimization by chemical and physical means.

The project has three components: (1) synthesis and crystal growth of new phases; (2) spectroscopic, crystallographic, and theoretical characterization of the new phases; and (3) time-resolved synchrotron studies of the molecular dynamics on photo-excitation. The time-resolved studies are to concentrate on complexes with transition metal containing chromophores, following our recent studies on geometry changes on excitation of such complexes.

The time-resolved experiments make use of polychromatic synchrotron radiation at the Advanced Photon Source. Our recent advances in the collection and processing of polychromatic Laue data have increased the accuracy of the time resolved synchrotron data to less than 0.01 Å.

Next Generation Semiconductors for Solar Water Splitting

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

PROGRAM SCOPE

Solar photoelectrolysis— the use of an illuminated semiconductor to split water into hydrogen fuel and oxygen gas—could potentially play an important role in enabling a clean energy economy since this technology offers the potential to renewably generate energy in the form of a portable chemical fuel that can be readily stored and transported in large quantities. At the point of use, hydrogen can either be converted into electricity with high efficiency using a fuel cell, burned like natural gas, or converted into traditional carbon-based fuels using Fischer-Tropsch reactions. However, solar photoelectrolysis is not yet a viable technology due to the low overall efficiencies (<1%) of the best materials currently available. This project has the goal of understanding and overcoming the efficiency limitations of some complex oxide and oxynitride semiconductors that have recently been discovered to have visible-light-absorbing medium band gaps, yet which still retain the hydrogen reduction ability of larger band gap materials like TiO_2 (which utilizes a far smaller portion of the solar spectrum that does not include visible light). These complex semiconductors will be grown as single crystals and/or crystalline thin films to enable accurate measurements of fundamental semiconductor properties (including absolute absorption coefficient, resistivity, carrier mobility, and carrier concentration) and photoelectrochemical activity. These samples will also be utilized for surface science measurements to determine the termination and atomic arrangements at their surfaces and to quantitatively assess the surface binding of molecules that are precursors, intermediates, or products of water splitting reactions, offering insights into water splitting reaction mechanisms.

FY 2012 HIGHLIGHTS

Epitaxial thin films of a quaternary oxynitride have been prepared on top of both optically transparent and electronically conductive substrates. Spectral ellipsometry has been utilized to determine the thickness and full optical constants of both the oxynitride thin film and the two substrates, proving that this oxynitride absorbs light very strongly. Initial experiments elucidating the influence of synthesis conditions on oxynitride film thickness and quality have been carried out, resulting in the controlled production of films 150 to 2500 nm thick. Techniques for measuring film resistivity and carrier concentration have been tested, giving preliminary estimates of their values for this system and providing a mechanism for monitoring their evolution across different synthetic conditions. The oxynitride film and both substrates have been characterized using standard surface science techniques.

Fundamental Studies of Energy- and Hole/Electron-Transfer in Hydroporphyrin Architectures

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Funding:	\$220,000

PROGRAM SCOPE

The long-term objective of the Bocian/Holten/Lindsey 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 synthetic goals (Lindsey research) include the preparation of multipigment arrays containing porphyrins and/or hydroporphyrins for (1) determination of the rates of ground-state hole/electron transfer as a function of array size, distance between components, linker type, site of linker connection, and frontier molecular orbital composition; and (2) examination of excited-state energy transfer among hydroporphyrins in multipigment arrrays, including both pairwise and non-adjacent transfer, with a chief aim to identify the relative contributions of through-space (Förster) and through-bond (Dexter) mechanisms of energy transfer, including the roles of site linker connection and frontier molecular orbital composition. In addition, we are preparing diverse bacteriochlorins bearing substituents at designated sites, with the goal to elucidation of the role of substituents in tuning the spectral and electronic properties of bacteriochlorins, with a primary aim of learning how to shift the long-wavelength absorption band deeper into the near-infrared region.

FY 2012 HIGHLIGHTS

We completed our studies of the metalation of bacteriochlorins, a project that was first initiated in 2005. The scope of metalation (via NaH or LDA in THF) is as follows: (a) for bacteriochlorins that bear two electron-releasing aryl groups, M = Cu, Zn, Pd, and InCl (but not Mg, Al, Ni, Sn, or Au); (b) for bacteriochlorins that bear two carboethoxy groups, M = Ni, Cu, Zn, Pd, Cd, InCl, and Sn (but not Mg, Al or Au); and (c) a bacteriochlorin with four carboethoxy groups was metalated with Mg (other metals were not examined). Altogether, 15 metallobacteriochlorins were isolated and characterized. The photophysical properties (fluorescence yields, triplet yields, singlet, and triplet excited-state lifetimes) of the zinc bacteriochlorins are generally similar to those of the metal-free analogues, and to those of the native chromophores bacteriochlorophyll *a* and bacteriopheophytin *a*. The availability of diverse metallobacteriochlorins should prove useful in a variety of fundamental photochemical studies and applications.

Bio-Inspired Electro-Photonic Structure for Dye-Sensitized Solar Cells

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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, that 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. The first is 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 allows 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. The second development is 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 these two independent technologies will allow us great latitude to understand and ultimately control the optoelectronic properties of the dye sensitized photoanodes.

FY 2012 HIGHLIGHTS

We have focused on two aspects of the growth of TiO_2 ”corn-field” by pulsed laser deposition (PLD), achieving 6.7% efficiency in relatively thin flat devices. Regarding the structure, we have established a method to control the growth of our tree-like structures by “seeding” them in precise locations via nano-patterning of conductive oxide features where, in subsequent depositions, the porous TiO_2 “blooms” out it in a bush-like fashion. In the coming period, we will move toward using this controlled growth and intrinsically better oxide to build devices with patterns supported by electro-photonic modeling.

Metal-to-Ligand Charge Transfer Excited States on Surfaces and in Rigid Media: Application To Energy Conversion

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Funding: $190,000

PROGRAM SCOPE

Focus 1: Electropolymerized Films for Optical, Membrane, and Catalytic Applications

Electropolymerization– polymerization at the surface of an electrode induced by an applied potential– is being exploited to produce thin films of electro- and/or photochemically-active polypyridyl complexes on electrode and semiconductor surfaces. This well-established, and useful, technique was first developed at UNC in a Meyer-Murray collaboration and is based on reductive polymerization of vinyl-derivatized polypyridyl complexes or oxidative polymerization of pyrrole-containing complexes. In contrast to other attachment strategies, which involve direct bonding to the electrode, electropolymerization has the advantage of not requiring surface modification and can be applied to any conducting substrate regardless of surface composition or morphology including functionalization of high surface area carbon electrodes. Film thickness can be controlled by controlling polymerization conditions. These techniques have been used to form thin, multi-layered structures containing single-site ruthenium and other metal complexes including precursors to known catalysts in solution for electrocatalyzed water oxidation or CO_2 reduction.

Focus 2: Photophysics and Photochemistry in Semi-Rigid PEG-DMA films

Polymerization of poly(ethyleneglycol)dimethacrylate (PEG-DMA) fluids provides a means for preparing thin (mm to cm), chemically inert PEG-DMA films that are optically transparent throughout the visible region of the spectrum and are conformable on the nanoscale. Polymerization with added Ru(II) polypyridyl complex light absorbers and electron or energy transfer donors or acceptors provides a basis for investigating electron and energy transfer dynamics in the semi-rigid environment of the films.

FY 2012 HIGHLIGHTS

We have demonstrated the successful electropolymerization of stable Ru(II) single site precursor catalysts for water oxidation and carbon dioxide reduction by reductive electropolymerization of vinyl-derivatized polypyridyl ligands. The coordination chemistry of the film-based complexes can be manipulated systematically by oxidative cycling to Ru(III) and, reductively, by electron addition to π^* levels on the polypyridyl ligands.

Energy transfer quenching of the Metal-to-Ligand Charge Transfer (MLCT) excited state $Ru(bpy)_3^{2+*}$ (bpy is 2,2’-bipyridine) occurs by added anthracene derivatives in PEG-DMA films containing nine ethylene glycol spacers (PEG-DMA550). Both slow, minority, diffusional and rapid, dominant, fixed-site energy transfer occur, the latter by the Dexter energy transfer mechanism as shown by the distance dependence of quenching. In films containing added methylviologen dication (MV^{2+}) as electron acceptor, excitation of the complex is followed by anthracene quenching, long-range ^{3}An- to An energy transfer migration, and ^{3}An- reduction of MV^{2+} to MV^+ with a net electron transfer distance of >90 Å!

Approaches to Integrated Photochemical Systems for Solar Energy Conversion

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PROGRAM SCOPE

This project investigates three related directions critical to developing a fundamental understanding of how to design and prepare integrated artificial photosynthetic systems for solar energy conversion. (1) We are investigating new approaches to light harvesting and photodriven charge generation using insights we have developed regarding multi-step electron transfer within fixed-distance donor-acceptor molecules in solution to address the analogous, but far more complex fundamental issues that arise in optimizing photodriven charge generation and transport in molecular solids relevant to artificial photosynthesis and molecular photovoltaics. (2) We are investigating the fundamental structural, electronic, and energetic requirements for integrating efficient light harvesting and photodriven charge separation in self-ordered molecular assemblies (SOMAs) with a strong emphasis on developing ordered solid state charge transport conduit structures for artificial photosynthesis and molecular photovoltaics. (3) We are investigating the fundamental structural, electronic, and energetic requirements for integrating photochemical charge separation systems, including SOMAs with benchmark multi-electron, multi-metallic catalysts for CO_2 reduction to solar fuels.

FY 2012 HIGHLIGHTS

We have developed thin, polycrystalline solid films in which photogenerated singlet excitons fission to generate two triplet excitons in high yield. Our results indicate that several rylene-based chromophores are energetically well-suited to provide two triplet excitons for every photon absorbed. The challenge is to develop tailored molecular systems by design that can use these excitons to separate charge efficiently.

We have developed a new SOMA based on a symmetric tetrabenzoporphyrin electron donor chromophore that absorbs sunlight strongly across the entire visible spectrum and has four perylenediimide electron acceptor dye molecules attached to it. This molecule self-assembles to form segregated stacks of donors and acceptors. Photodriven, single-step, intramolecular electron transfer in this system leads to long-lived charge separation in which the segregated stacks of donors and acceptors serve as charge conduits for electrons and holes. We are currently investigating how to orient thin solid films of this system and related molecules on substrates relevant to photovoltaics.

Chemical Control of Charge Trapping and Charge Transfer Processes at the Organic-Inorganic Interface with Quantum Dot Organic Complexes

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Funding:	$150,000

PROGRAM SCOPE

The overall goal of this research program is to map the chemical structure of the interface between a colloidal semiconductor nanocrystal (quantum dot, QD) and an organic molecule to the electronic processes that occur at this interface. These electronic processes include heterogeneous (QD to molecule) charge transfer, electronic passivation of surface trap states, and orbital mixing that creates new charge transfer-type interfacial states. Control of these processes by adjusting the surface chemistry of the QDs allows us to perturb the optical absorption or fluorescence spectrum of the QD-organic complex and/or the dynamics of the excited state of the QD-organic complex, and thereby determine the pathways by which electronic energy, input by light, decays and couples to the local environment of the QD.

FY 2012 HIGHLIGHTS

Our DOE-sponsored research this year has focused on three areas: (1) determination of mechanisms of nucleation and growth of quantum dots in an effort to develop reproducible syntheses with pure reagents, (2) use of photoinduced electron transfer as a probe of the adsorption geometries of redox-active molecules on the surface of quantum dots, and (3) investigation of the electronic structure of strongly coupled quantum dot-electronic complexes. In area (1), we reported control of the competition between step-growth and living chain-growth polymerizations in the formation of cadmium chalcogenide QDs from semiconductor clusters by varying the concentration of anionic surfactant in the reaction mixture. Chain-addition produces QDs over a larger range of sizes with better size dispersity than step-addition. Tuning the molar ratio of surfactant to the limiting ionic reagent allows for stoichiometric control of QD radius without relying on reaction time. In area (2), we used ultrafast transient absorption to determine that the rate constant for photoinduced electron transfer from colloidal CdS quantum dots (QDs) to alkylcarboxylate-functionalized viologens is independent of the number of methylene groups in the alkyl chain. The insensitivity of the electron transfer rate constant to the length of the functional groups on the viologen suggests that a “through-space” pathway, where the electron bypasses the alkylcarboxylate and tunnels instead through only the orbitals of the QD and of the bipyridinium core, is the dominant PET pathway. In area (iii), we described a method to control the quantum confinement and, therefore, the energy of excitons in CdSe QDs through adsorption of the exciton-delocalizing ligand phenyldithiocarbamate, PTC, and *para*-substitutions of the phenyl ring of this ligand with electron-donating or withdrawing groups. These substitutions control exciton delocalization in the QDs through the energetic alignment of the highest occupied orbitals of PTC with the highest density-of-states region of the CdSe valence band, to which PTC couples selectively.

Fundamental Studies of Light-Induced Charge Transfer, Energy Transfer, and Energy Conversion with Supramolecular Systems

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Funding:	$180,000

PROGRAM SCOPE

This project seeks to exploit supramolecular chemistry to (1) interrogate and understand fundamental aspects of light-induced charge transfer and energy transfer, and (2) 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 DSC environments.

Of greatest interest are dyes and shuttles that may lead, in combination with a separately developed interface and overall photo-electrode structures, to new or improved pathways for key component processes, including electron injection, shuttle diffusion, and charge collection, while inhibiting undesirable light-loss and/or charge-recombination processes. If we are fully successful, we will have (1) identified and validated useful new approaches to managing charge-flow, (2) synthesized and investigated the behavior of new shuttles and dyes that can effectively capitalize on the proposed new approaches, and (3) corralled appropriate combinations of new molecules and approaches to achieve light-to-electrical energy conversion with exceptionally high overall efficiency, or obtain the atomic-, molecular-, and system-, or sub-system-level insight necessary for others to be able to design, build, and understand superior dye-sensitized solar cells.

FY 2012 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 reported the first example of directional, long-distance energy migration within a MOF.

New redox shuttles based on macrocylic complexes of Cu(I) and Cu(II) have been examined. In these systems, desired dark-current-suppression/back-ET-inhibition is achieved via oxidation-state dependent coordination and release of a solvent molecule or auxiliary ligand. These systems lack the high-driving-force requirements of the iodide/tri-iodide system, as well as its corrosiveness and its undesirable propensity to associate with highly polarizable organic light-harvesters. Furthermore, the copper shuttles are more stable than the archetypal fast redox shuttle, ferroecene$^{+/0}$, and diffuse faster than *tris*-polypyridyl cobalt shuttles.

Light-Driven Charge Transfer in Face-to-Face Donor-Spacer-Acceptor Supramolecular Systems

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Funding:	$180,000

PROGRAM SCOPE

During the past decade, significant progress has been made in elucidating the mechanism, dynamics, and efficiency of photoinduced charge transfer in DNA. DOE-supported experimental studies conducted by the Lewis group have provided the first direct measurements of the distance-dependence of the dynamics and efficiency of hole (positive charge) transport across well-defined DNA base pair sequences. Hole transport in repeating adenine or guanine sequences has been shown to occur via a random walk mechanism with base-to-base hopping times of ca. 1 nanosecond. However, significant experimental and theoretical challenges remain. The efficiency of charge separation in DNA is limited by the competition between the relatively-slow hole hopping process and energy-wasting charge recombination. In addition, the dynamics of excess electron transport processes in DNA remain to be established. Studies currently in progress address these challenges. These studies employ donor-bridge-acceptor systems possessing chromophores separated by bridging base pair domains of variable length, base pair sequence, and base structure. The efficiency of charge separation and the dynamics of charge separation and charge recombination are determined by means of transient absorption spectroscopy on the femtosecond to millisecond time scales. Methods of increasing the efficiency of charge separation via hole transport will be explored. These include increasing the rate constants for hole hopping by chemical modification of the DNA structure and decreasing the rate constants for charge recombination by appropriate selection of the chromophores used for photoinduced charge separation. Parallel studies will be directed at obtaining the first direct measurements of the dynamics and efficiency of excess electron transport in DNA.

FY 2012 HIGHLIGHTS

Recently there has been growing interest in determining the effects of alteration of the oligonucleotide bases or sugar-phosphate backbone on the dynamics of electron transfer in DNA. We have suggested that enhanced hopping rates for poly(7-deazaadenine) vs. adenine in a diblock purine system might be a consequence of increased conformational mobility resulting from the removal of the 7-amino group from the major groove. Among the backbone modifications that have drawn attention as alternatives to the locked nucleic acids (LNA), we find that the rate constant for base-to-base hopping in LNA G-blocks or A-blocks is only slightly slower than that for unmodified DNA. Slower hopping rate constants are accompanied by lower quantum yields for charge separation.

Radiation and Photochemistry in the Condensed Phase and at Interfaces

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Funding: $3,850,000

PROGRAM SCOPE

Current research at the Notre Dame Radiation Laboratory addresses the basic science underpinning fundamental advances in radiation chemistry, solar energy conversion, and applications in the areas of nuclear energy and the biochemical sciences. The first tackles both energy deposition and transport following the impact of ionizing radiation on condensed media and also structure, properties, and reactions of the resulting radicals. The second focuses on understanding photo-induced charge separation and excited-state dynamics in semiconductors, conducting polymers and carbon nanostructures with the ultimate goal of delivering improved efficiencies for solar energy capture and conversion. The third highlights the important role of radiation chemistry throughout the nuclear power generation process, from reactor chemistry through waste separation and storage. The fourth, a new direction, leverages our extensive in-house experimental and theoretical radiation chemistry expertise, unique instrumental constellation, and strong local, national, and international collaborative networks. It addresses specific challenges in the biochemical arena, for example, investigating energy flow in natural photosynthetic systems, dissociative electron attachment to biomolecules, and radiation damage incurred during macromolecular crystallography.

FY 2012 HIGHLIGHTS

An explanation for the large gas-to-liquid shift and temperature dependence of the UV absorption spectrum of liquid water was uncovered through calculations on disparate hydrogen bonding motifs in selected water clusters. Strong resonant features observed upon electron attachment to alkyl and aryl triflates enabled reliable identification of dissociation mechanisms. Various reactive species in novel non-thermal atmospheric plasma jets were identified by UV/optical emission spectroscopy.

By sequentially assembling CdSe quantum dots and squaraine dyes onto TiO_2 films, energy and electron transfer processes were successfully coupled to generate photocurrent in a quantum dot solar cell. Careful anchoring of semiconductor and metal nanoparticles on reduced graphene oxide with both site and spatial selectivity enabled the manipulation of photoinduced energy and electron transfer processes in photocatalytic and photovoltaic assemblies. Quantum confinement and environmental effects on charge and exciton dynamics of low-dimensional nanostructures were resolved using transient absorption microscopy.

Temperature programmed desorption revealed two types of chemisorbed water on the surface of iron oxide nanoparticles. Irradiation of these oxides led to comparatively little production of molecular hydrogen, indicating their relative radiation inertness. Determination of a key equilibrium constant at high temperatures, linking hydrogen atoms with hydroxyl radicals, allowed the first successful modeling of the radiation-induced chemistry of radicals in the cooling loops of pressurized water reactors.

High-resolution mapping of cofactor-specific photochemical function in photosynthetic reaction centers was achieved by polarization-selective ultrafast spectroscopy in single crystals at cryogenic temperature. A universal amide bond-cleavage mechanism was identified in X-irradiated peptide films, and peptide chemisorption of small peptides onto gold surfaces was demonstrated. The reasons for conflicting literature results on scavenger efficacy in mitigating radiation damage during macromolecular crystallography were clearly identified.

Photovoltaic and Photochemical Properties of Conjugated Ionomer Junctions

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PROGRAM SCOPE

The primary goal of this project is to understand the photovoltaic and photochemical properties of new types of organic junctions based on asymmetries in ionic or electronic carrier populations. Both of these sources of asymmetry differ from the conventional frontier-orbital offsets that currently dominate organic photovoltaic systems. The electronic carrier asymmetry approach is equivalent to the p-n junction found in crystalline silicon photovoltaics, and the ionic carrier asymmetry approach is an intriguing analogue where charge depletion due to ion, rather than electron, exchange is possible. It is perhaps not surprising that systems with frontier-orbital offsets dominate studies of organic systems because of their effectiveness in separating excitons. The challenges facing the fabrication of true organic p-n junctions have also helped maintain that focus. In our work, we have overcome barriers to the fabrication of conjugated polymer p-n junctions by using ion-functionalized conjugated polymers (conjugated ionomers or polyelectrolytes), and we have also demonstrated how the combined presence of ionic and electronic carriers in conjugated ionomers can lead to interesting photochemical processes.

FY 2012 HIGHLIGHTS

We have used an electrochemical method we developed to make interfaces between reductively (n-type) and oxidatively doped (p-type) conjugated ionomers with systematically varying dopant densities. Studies of these interfaces demonstrated that conjugated ionomer p-n junctions are distinct from classic inorganic p-n junctions in that they exhibit neither the voltage-dependent capacitance of a semiconductor depletion layer nor the classic Shockley, diffusion-based current-voltage behavior. Variation of the ionic functional group and dopant density enabled the current-voltage behavior to be tuned from symmetric to asymmetric with equilibrium exchange current densities varying by over six orders of magnitude. Under illumination, open-circuit voltages near 0.5 V were observed despite the absence of any substantial offset in frontier orbital positions of the constituent materials. In studies of the basic photochemistry of conjugated ionomers, we demonstrated the remarkable ability for ionic functionality to stabilize the charge transfer complex formed between oxygen and a range of conjugated polymer backbones, and highlighted its implications to the long-term photochemical stability of conjugated polymers.

Semiconductor-Electrocatalyst Contacts: Theory, Experiment, and Applications to Solar Water Photoelectrolysis

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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 2012 HIGHLIGHTS

This research program started July 15, 2012. In the first months, we have started experiments to probe the interface between catalysts and semiconductors and started the development of computer simulations. Both efforts are proceeding smoothly, and we expect publication of our initial results in the next period.

Molecular and Structural Probes of Defect States in Quantum Dots for Solar Photoconversion

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Funding:	$185,000

PROGRAM SCOPE

The objective of this research on quantum confined nanocrystals is to develop a fundamental understanding of the chemical properties of ligand-nanocrystal interfaces that will enable the control of defect-driven charge recombination in these systems. With this control, quantum confined nanocrystals may represent a cost effective means of absorbing light over the full solar spectrum for the production of electricity and fuels from sunlight. New spectroscopic techniques will be developed in this project that allow a direct correlation of molecular structural information about the ligand-nanocrystal interactions with the corresponding density and energetic distribution of surface defects and the influence that these defects have on charge transport and recombination. The insight that is gained will provide a molecular basis for the rational development of novel pathways for the of use quantum dots in systems for solar energy transduction.

FY 2012 HIGHLIGHTS

We have successfully constructed spectroelectrochemical sample structures with ligand exchanged lead sulfide quantum confined nanocrystals sandwiched between two electrodes. One electrode is semi-transparent in the infrared spectral region while the other is reflective. We have succeeded in our initial efforts to measure ultrafast infrared transient absorption signals from the ligand exchanged lead sulfide nanocrystals in these samples. In the next period, we will fully characterize the electrochemical and optical properties of the lead sulfide nanocrystals and combine the new sample capabilities with ultrafast infrared spectroscopy to explore mechanisms of charge carrier hopping, transport, and recombination among nanocrystal assemblies of well-defined electronic structure and molecular composition.

Nanostructured Photocatalytic Water Splitting Systems

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PROGRAM SCOPE

This project investigates fundamental problems associated with visible light-driven water splitting in molecular photocatalytic 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 2012 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 TiO_2 electrodes. One of the major problems with this system is that back electron transfer between TiO_2 and the oxidized dye is faster than electron transfer from the water oxidation catalyst to the dye. In Photosystem II, the analogous electron transfer is mediated by a tyrosine-histidine relay. The insertion of a high potential benzimidazole-phenol (BIP) mediator—synthesized by the Moore-Gust team at Arizona State—into the TiO_2-dye-IrO_2 system results in an enhanced bleaching recovery rate of the dye and an increase in the quantum yield for water splitting by a factor of two.

In photoelectrochemical water splitting, proton management can be a significant problem, especially when using earth-abundant catalysts that function near neutral pH. Experiments were done to quantify the losses associated with series resistance and membrane polarization in electrolysis cells that mimicked effcient water splitting cells at solar current density. A potential solution to the membrane polarization problem—which can result in losses of 500 mV or more—was found for both anion- and cation-exchanging membranes.

Physical Chemistry Reaction Dynamics in Ionic Liquid

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Funding:	$175,000

PROGRAM SCOPE

This research is part of a small group grant shared by Blank, Castner, Margulis, Maroncelli, and Wishart. It is focused on deriving a fundamental understanding of ionic liquids as reaction media. Ionic liquids are a relatively new class of materials comprised solely of ions. They differ from the molten salts long known in inorganic chemistry by being constructed from a combination of bulky organic and inorganic ions which serve to depress the melting points below 100°C (and often below room temperature). Ionic liquids are currently being explored for use in a wide variety of applications, many of which include energy transduction and storage technologies relevant to DOE's mission. The basic research undertaken here is meant to provide a fundamental basis for applications of ionic liquids in energy technologies. Different members of the team study ionic liquid structure, non-reactive transport of molecular solutes and electrons, and homogeneous electron transfer reactions in this new medium. The Maroncelli group effort has consisted of experimental measurements of solute diffusion using NMR techniques and solvation dynamics and bimolecular electron transfer reactions using ps/fs time-resolved emission spectroscopy.

FY 2012 HIGHLIGHTS

We completed a number of projects initiated at the inception of this grant. One project involved fluorescence quenching measurements and modeling of bimolecular electron transfer, which was published in 2012. This work served to answer the question of why diffusion-limited electron transfer reactions appeared to be anomalously fast in ionic liquids. We found this anomaly to result primarily from the use of the simplified reaction models often used with success in low-viscosity conventional solvents but inapplicable in the high-viscosities prevalent in ionic liquids. In other studies, we employed fs/ps time-resolved emission techniques to observe the complete solvation response to a reported solute in 21 ionic liquids and two ionic liquid + conventional solvent mixtures. The results in the neat ionic liquids enabled us to test the applicability of dielectric continuum theories of solvation in ionic liquids. This work, now in press, should provide the benchmark data for further development of theories of ionic liquid solvation. Experimental work on the mixtures is also complete and is currently in draft form. Finally, we have completed NMR measurements of the diffusion coefficients of a variety of solutes in a homologous series of ionic liquids. These data, combined with literature data from a variety of other sources, provides an overview of the similarities and differences between diffusion in ionic liquids and conventional solvents as well as a start to being able to predict diffusion rates in ionic liquids. A manuscript on this work will be submitted shortly.

Photoelectrochemical Conversion of Carbon Dioxide to Methanol and Higher Order Alcohols

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

PROGRAM SCOPE

One route to solar-based liquid fuels is the photoelectrochemical conversion of CO_2 to alcohols using a light responsive, electrochemical cell based on a p-type photocathode. The research proposed here is based on our finding that a p-GaP electrode in the presence of aqueous pyridinium (pyH^+) and irradiated with visible or near UV light produces methanol at or below the cell's short circuit potential. Thus, this system directly converts light energy into a chemical fuel. The work proposed here seeks to (1) develop an understanding of the CO_2 reduction mechanism in the electrode/pyH^+ system so that it can be exploited to produce a practical photoelectrochemical route to methanol, (2) optimize the catalytic nature of the semiconductor/pyridinium interface in terms of faradaic yield and optical conversion efficiency, and (3) maximize the concentration of CO_2 present at the electrode-electrolyte interface thereby enhancing the observed reaction rate.

It is hypothesized that the key reaction intermediate in the CO_2 conversion process is a radical carbamate species generated by the reaction of one-electron reduced pyH^+ (pyridinyl) and CO_2. This species will be sought using modern electroanalytical and photoelectrochemical methodologies in combination with spectroelectrochemical techniques including in situ epr and Raman spectroscopies. Both metal and semiconductor electrodes will be employed to obtain the required electroanalytical and spectroelectrochemical data. Once a specific mechanism and electrochemical construct is available, the electrocatalytic response of the system will be optimized. It will be important to enhance both the rate of the electrodic reaction and the overall electrochemical yield. Reaction kinetics will be improved by considering the details of the interfacial charge transfer.

FY 2012 HIGHLIGHTS

Research over the past year has focused on the photoelectrochemical response of p-GaAs and p-InP for the reduction of CO_2 to a variety of organic products in the presence of a dissolved pyridinium catalyst. In addition, in order to directly model the initial steps and overall kinetics of the class of reactions that produces C_1 products, a study was undertaken using a platinum electrode interface. Our most important finding over this past year is that under certain conditions, carbon dioxide species can be coupled to produce carbon-carbon products. This coupling is dependent both on the aromatic amine catalyst employed and the semiconductor surface utilized. It also appears to be affected by the mass transport of CO_2 in the photoelectrochemical cell (though this finding is quite preliminary and continues to be studied). Pragmatically, we have developed a p-GaAs cell that reproducibly generates butanol, a readily recognized internal combustion engine fuel, in 10-20% faradaic efficiency under white light illumination.

Understanding Electronic and Atomic Requirements in Catalytic Water Oxidation

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Funding:	$150,000

PROGRAM SCOPE

Our research effort over this project period was primarily focused on the understanding of the structure and reactivity of the intermediates in the blue dimer (BD) di-Ru catalyst for water oxidation.

FY 2012 HIGHLIGHTS

We used a stop-flow/freeze-quench assembly to prepare reactive intermediates by oxidation of the BD catalyst with cerium ammonium nitrate (Ce(IV)). Controlled freezing of the reaction mixtures in msec to few seconds times allowed us to prepare samples of BD [4,5] and BD [3,4]-peroxo complexes (the oxidation states of the Ru centers are indicated in brackets). These samples were characterized by Ru K-edge XANES, EXAFS, and EPR.

For BD [4,5] we reproduced the EPR spectrum previously reported by J. Hurst, confirmed the oxidation states of Ru centers by Ru K-edge XANES, and detected the short Ru^V=O bond (1.70 Å) by Ru K-edge EXAFS. Using the effect of multiple scattering in the EXAFS, we also determined the Ru-O-Ru bond angle of 166±2° and the distance between Ru atoms of 3.71 Å. Experimentally, we observed the reactivity of

BD [4,5] towards water with formation of a BD [3,4]-peroxo intermediate. This intermediate has a distinct EPR signal, and assignment of the [3,4] oxidation state from Ru K-edge XANES is in good agreement with EPR.

We initiated resonance Raman analysis of the reactive intermediates. Measurements were done on frozen solutions of the BD [3,4] and [3,4]-peroxo intermediates. The resonance Raman spectrum of BD [3,4] is in agreement with the one previously reported by J. Hurst. The main spectral feature at 397 cm^{-1} corresponds to the symmetric Ru-O-Ru stretching mode. The Raman spectra of BD [3,4] prepared in regular and in ^{18}O enriched (98%) water are almost identical, showing that the bridging oxygen is not exchanged under experimental conditions and that the $Ru\text{-}OH_2$ and Ru-OH modes are not visible in the Raman spectrum. Spectra of the [3,4]-peroxo intermediate prepared in regular and ^{18}O enriched water demonstrated a prominent shift of the band at 683 cm^{-1} to 637 cm^{-1}. Trying to understand the factors controlling the BD [4,5] reactivity towards water, we performed ^{17}O labeling of the $Ru^V{=}O$ in BD [4,5]. In EPR, we were able to directly show a high spin density (via large ^{17}O hfs with A_{xx}=60 G) on the oxygen center consistent with the radicaloid character of the $Ru^V{=}O$ oxygen. The DFT prediction of a high spin density on the oxygen is in agreement with the experimental results. Singly occupied non-bonding MOs with a high contribution of oxygen p-orbitals are responsible for the high spin density.

Validations of Time-Resolved X-Ray Emission Spectroscopy for Analysis of Mn-Based Natural and Artificial Sunlight-to-Energy Assemblies

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Funding:	$124,000

PROGRAM SCOPE/HIGHLIGHTS

The goal of this project is to design miniature x-ray emission spectrometers capable of dispersive detection of x-ray emission spectra at Mn K alpha and K beta lines. We built two spectrometers of such type. With these spectrometers we tested the paradigm of “detection-before-destruction” on the example of a metalloprotein complex exposed at room temperature to the high x-ray flux typical of third-generation synchrotron sources. Following the progression of the x-ray-induced damage by Mn Kβ x-ray emission spectroscopy, we demonstrated the feasibility of collecting room temperature data on the electronic structure of native Photosystem II, a trans-membrane metalloprotein complex containing a Mn_4Ca cluster. The determined non-damaging observation timeframe (about 100 milliseconds using continuous monochromatic beam, deposited dose $1*10^7$ photons/μm^2 or $1.3*10^4$ Gy; and 66 microseconds in pulsed mode using pink beam, deposited dose $4*10^7$ photons/μm^2 or $4.2*10^4$ Gy) is sufficient for the analysis of this protein’s electron dynamics and catalytic mechanism at room temperature. Reported time frames are expected to be representative for other metalloproteins. The described instrumentation, based on the short working distance dispersive spectrometer, and experimental methodology is broadly applicable to time-resolved x-ray emission analysis at synchrotron and x-ray free-electron laser light sources.

Currently, we are designing an experiment to combine dispersive x-ray emission measurements with laser pump/x-ray probe set up for time-resolved analysis of changes in the electronic structure of the Oxygen Evolving Complex of Photosystem II.

Atomistic Time-Domain Simulations of Light-Harvesting and Charge-Transfer Dynamics in Novel Nanoscale Materials for Solar Energy Application

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Funding: $170,000

PROGRAM SCOPE

Fundamental mechanisms of solar energy harvesting and flow in novel nanoscale materials will be investigated in a series of theoretical studies with emphasis on simulation in real time, atomistic level, and direct connection with experiment. The state-of-the-art theoretical approaches developed in our group will be applied to several closely related systems that hold great promise for light harvesting, charge separation, and transport. With wealth of time-resolved experimental data on electron transfer (ET) in these systems, the mechanisms responsible for the ET and energy flow are only partially established and remain controversial. Our expertise in nonadiabatic molecular dynamics and time-domain density functional theory will allow us to address the fundamental aspects of the photo-excitation dynamics on the nanoscale. The proposed studies will result in a predictive framework for design of novel, efficient, and cost-saving solar cells (SC). Particular attention will be given to (1) electron transfer at interfaces between nanoscale materials, (2) photoinduced dynamics in novel nanoscale materials for solar energy harvesting, and (3) novel physical and chemical routes for control and enhancement of SC efficiencies.

Modular Nanoscale and Biomimetic Assemblies for Photocatalytic Hydrogen Generation

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Funding: $360,000

PROGRAM SCOPE

The successful utilization of the clean energy carrier hydrogen (H_2) as a fuel requires methods for H_2 production using primary energy sources not based on fossil fuels. Of possible primary energy sources, solar offers the greatest long-term impact because of its abundance and availability, but many challenges need to be met for its utilization. For the direct conversion of sunlight to stored chemical energy in H_2, efficient photochemical reduction of protons in water is needed. The overarching objective of this project is the development of a system to convert light energy into the formation of H_2. The system will consist of a multifunctional assembly that captures visible light and transfers photogenerated electrons to a catalyst at which proton reduction occurs. The assembly has a modular design that allows advances to be made on the modules in parallel by the participating PIs and facilitates addition of new functionality as the work progresses. The three modules are (1) photoactive biomimetic chromophores for photoinduced charge transfer, (2) carbon nanotubes for long-range charge separation, and (3) catalysts for H_2 production from water. This project draws from the fields of biochemistry, materials chemistry, and inorganic chemistry. For module 1, metalloporphyrin-peptides are being developed for use in attaching photoactive porphyrins to nanotubes for photoinduced charge transfer. In module 2, a membrane consisting of vertically-aligned carbon nanotubes is being utilized for long-range charge transfer from the porphyrin electron donor to the catalyst. The membrane also compartmentalizes the photochemical and catalytic modules. Module 3 consists of catalysts based on earth-abundant metals that produce hydrogen fuel from water. Progress on this project will advance the areas of nanotube chemistry, biomolecular engineering, and catalysis. In the long term, success in this project will yield a new approach to preparing materials capable of the storage of solar energy in the form of hydrogen fuel.

FY 2012 HIGHLIGHTS

We have reported a system using semiconductor nanocrystals and a soluble nickel catalyst for light-driven production of hydrogen from water. The system is highly robust, yielding >600,000 turnovers and quantum yields in water of over 36%. We also have successfully prepared nanotube membranes capable of electron transfer, and we have modified nanotubes with porphyrin-peptides and proteins as electron donors.

Photophysics and Photoinduced Charge Transport in Single Walled Carbon Nanotubes

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Funding:	$125,000

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. Our overall goal is to fully understand the energetics and dynamics of the photoexcited state in carbon nanotubes, a new material consisting of single sheets of graphene rolled into 1-nm diameter cylinders. The discoveries enabled by this project may lead someday to the development of new technologies based on nanotube photonics. For example, through the study of the photoluminescence properties of individual carbon nanotubes, we aim to determine the timescales and origins of radiative and non-radiative pathways for excited electrons in nanotubes. In a second aim, carbon nanotubes will be excited with ultrafast visible and UV laser pulses with the goal to generate (and detect) more than one excited electron via absorption of only a single photon, a process called “multiple exciton generation” (MEG). Through our proposed studies of carbon nanotube photophysics, we will (in the long term) address two fundamental intrinsic loss mechanisms that limit the efficiency of Si solar cells.

FY 2012 HIGHLIGHTS

We studied the theoretical energy limit threshold for MEG processes in carbon nanotubes through measurements of the excited state dynamics (i.e., Auger recombination dynamics) in nanotubes with specific structures and diameters. Preliminary analysis suggests that the Auger recombination time in carbon nanotubes is very fast, approximately 2 ps for the nanotubes studied. Interestingly, this value is almost double the value for nanotubes with smaller diameters, suggesting that structure will have a large effect on the efficiency of the MEG process. We also used correlated topographic and photoluminescence measurements of individual nanotubes using a new atomic force and optical microscope apparatus in order to understand the origins of their low photoluminescence efficiency. Surprisingly, only about 11% of all carbon nanotubes were found to be highly emissive, while approximately 36% of all nanotubes displayed much weaker luminescence. The remaining 53% of the nanotubes observed on the substrate did not have any observable photoluminescence emission. Our data suggest that the low ensemble photoluminescence efficiencies for carbon nanotubes can be largely attributed to a small percentage of bright nanotubes in the ensemble, and not to a large population of poorly emitting nanotubes. Future experiments will determine the fraction of bright nanotubes for species that have been intentionally brightened by small molecule additives, thus giving a theoretical maximum photoluminescence efficiency for an ensemble.

Nano-Structured Electrocatalysts for Conversion of Solar Energy to Fuels

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Funding:	$250,000

PROGRAM SCOPE

Our goals include finding new materials and/or morphologies that facilitate light absorption and charge transfer regarding solar photoelectrochemistry. This frequently involves searching for new photomaterial synthesis strategies. We are currently exploring the growth of materials via several techniques. The first is a reactive ballistic deposition, a technique in which the materials are evaporated onto a substrate through a low-pressure reactive gas (e.g., oxygen). The gas reacts with the evaporating species once it adsorbs on the surface (e.g., Ti would react with oxygen to create TiO_2). If the evaporating species are deposited at a glancing angle, self-shadowing can occur leading to nanostructured surfaces. In a second technique, we are exploring hydrothermal and solvothermal growth of different materials including Ta_2O_5, TiO_2, and Fe_2O_3. Additionally, we are studying spray pyrolysis and electrodeposition techniques for growth of high quality nanostructured metal-oxide semiconductors. Finally, we are also studying composite materials (e.g., Zn/WO_3, $Bi_2O_3/PbMoO_4$) that can improve the photocurrent for water splitting by rapid screening via scanning electrochemical microscopy (SECM).

FY 2012 HIGHLIGHTS

We have studied BiOI (bandgap 1.8 eV) and BiSI (bandgap 1.6 eV) nanostructured films deposited by spray pyrolysis for photooxidation of water and found that both materials exhibit good performance but are very unstable in aqueous solution. Thus, if ultrathin transparent protective layers could be found and easily applied, these materials would be promising candidates for solar water oxidation. We also made inroads into increasing the visible light contribution to the water oxidation performance of titania via (1) a new hydrothermal synthesis method that yields single-crystalline nanowires of exceptional small cross-section and (2) co-treating the nanowires with ammonia and hydrogen to increase the light absorption in the visible region. Here, the small cross sections of the wires allow for better "doping" of the titania. We employed reactive ballistic deposition to simultaneously deposit four materials to synthesize Mo and W doped $BiVO_4$ and confirmed earlier results from the Bard group regarding the large increase in water oxidation performance with these dopants. We studied p-type $CuBi_2O_4$ films that were electrodeposited for water reduction but found these films to be unstable in an acidic environment and more stable in a basic environment. Rapid screening SECM allowed us to test the photocurrent response of various metal oxide composites. Via this rapid screening technique, we test the photocurrent response of 25 different metal dopants into WO_3 each at 5 different concentrations. We found that a 9%Zn/WO_3 composite can increase the photocurrent for water oxidation by 2.5 times over that of bare WO_3 which was the best of all samples tested. We also found n-type Bi_2O_3/p-type $PbMoO_4$ composite material that can improve the stability and photocurrent for proton reduction.

Light Induced Energy and Electron Transfer Reactions of Photoactive Transition Metal Complexes

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Funding:	$150,000

PROGRAM SCOPE

Over the past few years, the work of the Schmehl group has focused on understanding energy migration in light harvesting complexes of Ru(II) and Os(II). The approach to making extended light harvesting systems is via generation of block copolymers of Ru(II) and Os(II) chromophores using atom-transfer radical polymerization. When created on surfaces, this approach should allow for development of energy gradients that will serve as effective solar energy collectors. The development of a considerably simpler procedure for making effective light harvesting ensembles is the desired objective.

Another objective proposed for the next three years is the detailed investigation of the photophysics and 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. This strategy of having a one electron light induced reaction coupled to lead to the production of two electron oxidation and two electron reduction products may potentially lead to viable thermal or photochemical catalysts for net two electron chemical transformations.

The group is also devoting significant effort to the exploration of first row transition metal clusters (nanoparticles) as catalysts for hydrogen generation. Using expertise in the study of light induced electron transfer reactions of transition metal complexes, we are able to make systems having sacrificial electron donors that provide, upon photolysis, a constant supply of electrons to nanoparticulate catalysts.

FY 2012 HIGHLIGHTS

The Schmehl group illustrated highly exacting control, via manipulation of pH, of intramolecular excitation energy transfer processes in aqueous solution (*Journal of the American Chemical Society*, 2012). In a system where excited state energy can reversibly shuttle between a pyrene chromophore triplet excited state and a Ru(II) complex metal-to-ligand charge transfer state, the equilibrium location of the excitation energy depended on the pH of the surrounding environment. This behavior allowed development of unique sensors for singlet oxygen under hypoxic conditions.

The group has also developed detailed protocols for determining the efficiency of hydrogen generation catalysts under solar (or simulated solar) photochemical conditions. The work employs a simple photochemical system that delivers electrons, with a clearly defined efficiency, to water reduction catalysts. With this system, it is possible to (1) determine the quantum efficiency of catalysts for hydrogen generation and (2) provide direct comparison of different catalysts under similar conditions. The work, currently under review for publication, initially focused on evaluating a newly developed Co(III) catalyst for water reduction.

Photoinitiated Electron Collection in Mixed-Metal Supramolecular Complexes: Development of Photocatalysts for Hydrogen Production

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Funding:	$134,000

PROGRAM SCOPE

This project aims to explore the fundamental science important for the absorption of solar light, use of this light to provide the driving force for intramolecular electron transfer and electron collection, and the reduction of water to produce hydrogen fuel in supramolecular assemblies. The complexity of these tasks requires the control of many stepwise processes on a molecular level to achieve high efficiency and turnover for solar harvesting molecules. The focus is on the use of metal centers for the collection of reducing equivalents in order to allow facile delivery of these reducing equivalents to a water substrate the produce hydrogen fuel.

Classes of mixed-metal supramolecular complexes have been designed, developed, and studied with promising redox and excited state properties. These systems couple charge transfer light absorbing metals to reactive metals such as rhodium(III) that will allow these systems to undergo photoinitiated electron collection (PEC) while possessing reactive metal sites capable of delivering collected electrons to a substrate such as H_2O to facilitate the production of H_2. The factors impacting multi-electron photochemistry and the reduction of water to produce H_2 are explored, aimed at providing a detailed understanding of the mechanism of action of these unique photocatalysts and the factors that impact functioning.

FY 2012 HIGHLIGHTS

Demonstrated this project period is the development of photocatalysts with good efficiency for the absorption of light, the collection of reducing equivalents, and the catalysis of water reduction in a single molecule. Work has uncovered some important design constraints to control the photoinitiated electron collection (PEC) and catalysis of water reduction by supramolecular complexes. The study of impact of sub-unit variation has allowed for basic science knowledge that is further translated to increased efficiency. It is shown that orbital inversion in these supramolecules occurs with minor changes in design and that orbital energetics is critical to control for PEC. It has been demonstrated that the steric protection of the photoreduced metal center is paramount to the demonstration of PEC and water reduction catalysis. A careful balance of sterics and electronics has allowed the development of new bimetallic water reduction photocatalysts for the light initiated electron collection and catalysis of hydrogen production. New collaborations have been established to explore the complicated photophysics of these promising photocatalysts in more detail. New structural motifs for the photoinitiated reduction of water to produce hydrogen fuel using solar light have been designed, and initial members of these series prepared and studied. This is uncovering more complexity into the role of sub-units on the redox, spectroscopic, photophysical, and photocatalysis by supramolecular complexes, including unexpected impacts from terminal ligand variation.

Membrane-Organized Chemical Photoredox Systems

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Funding:	$130,000

PROGRAM SCOPE

The project has two interrelated objectives: (1) to identify chemical principles that regulate water oxidation catalysis and (2) to explore the use of microphase-organized assemblies in biomimetic approaches to solar-driven water photolysis. In pursuit of objective 1, we have been developing advanced EPR techniques and DFT-based theoretical methods to characterize unstable species detected during O_2 evolution catalyzed by the ruthenium “blue dimer” ($[(bpy)_2Ru^V(O)]_2O^{4+}$, denoted {5,5}). In pursuit of objective 2, we have been investigating pyrylium ions as agents to drive photosensitized charge separation across closed bilayer membranes. We have previously shown that, in favorable cases, these ions can rapidly transport electrons across bilayers via a carrier-mediated electroneutral e^-/OH^- antiport mechanism. Our recent focus has been on coupling pyrylium-mediated transmembrane redox to reduction of compartmented reagents, including protons to H_2.

FY 2012 HIGHLIGHTS

(1) Water oxidation catalysis: We have concluded analyses by advanced EPR methods (ESEEM, HYSCORE, 1H ENDOR, PEANUT) of a paramagnetic signal formed during catalytic turnover of the above-referenced water oxidation catalyst. Results from this investigation, which represents the first study of its kind, indicate that the signal is not due to a bipyridine ligand-based radical, as previously thought, but rather is from a metal-centered S = ½ paramagnet which, in turn, could be either a chemically reduced species formed during water oxidation or a component of {5,5} in which the electron configuration about the

metals corresponds to a highly reactive Ru^{IV}-$O^{\bullet}$ di-radicaloid state. DFT calculations designed to assess possible non-innocence of the bipyridine ligands in catalyzed water oxidation are also being finalized for publication. One notable feature of this study is the development of a realistic solvation shell for the reactions under investigation; this feature will allow calculation of energetic barriers with an unusually high degree of confidence. Additional publications dealing with chemical reactions of the catalyst, including pulse radiolysis studies demonstrating facile bipyridine ring hydroxylation and studies demonstrating non-innocent participation of nitrate ion in chemically-driven water oxidation, are also forthcoming.

(2) Biomimetic transmembrane oxidation-reduction: We have concluded (and published) a study examining the prospects of using low-potential pyrylium ions to drive H_2 photoproduction in artificial photosynthetic membrane-based systems. Although we were able to achieve several performance goals in these assemblies, the photoconversion quantum efficiencies were very low. This appears to be a fundamental limitation imposed by the chemistry of the pyrylium ions themselves arising from kinetic factors associated with ring opening-closing cycling reactions upon which the device was based. Studies to assess the use of similar micelle-based systems to control these reactions (where ring opening/closing is not required) are ongoing.

Fundamental Studies of Energy- and Hole/Electron-Transfer in Hydroporphyrin Architectures

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Funding:	$165,000

PROGRAM SCOPE

The long-term objective of the Bocian/Holten/Lindsey 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 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 group), and electrochemical, electron paramagnetic resonance, and resonance Raman studies, as well as density functional theory calculations (Bocian Group). The proposed research encompasses four interrelated themes:

(1) determination of the rates of ground-state hole/electron transfer between (hydro)porphyrins in multipigment arrays as a function of array size, distance between components, linker type, site of linker connection, and frontier molecular orbital composition;

(2) examination of excited-state energy transfer among hydroporphyrins in multipigment arrrays, including both pairwise and non-adjacent transfer, with a chief aim to identify the relative contributions of through-space (Förster) and through-bond (Dexter) mechanisms of energy transfer, including the roles of site of linker connection and frontier molecular orbital composition;

(3) elucidation of the role of substituents in tuning the spectral and electronic properties of bacteriochlorins, with a primary aim of learning how to shift the long-wavelength absorption band deeper into the near-infrared region; and

(4) continued development of the software package PhotochemCAD for spectral manipulations and calculations through the compilation of a database of spectra for naturally occurring and synthetic hydroporphyrins. The availability of such data should augment efforts in the design of light-harvesting systems where spectral coverage in the red and near-infrared regions is desired.

Collectively, the proposed 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 characterization.

FY 2012 HIGHLIGHTS

The research in the Holten laboratory has led to the following advancements: (1) insights into molecular tuning of optical and photophysical properties of a large set of free base (metal free) bacteriochlorins; (2) photophysical properties and electronic structure of several sets of metallobacteriochlorins; (3) properties of the singlet and triplet excited states and photochemical stability of free base, zinc, and palladium dicyanobacteriochlorins and comparison with analogs that do not bear cyano-substituents; and (4) effects of substituents on the photophysical and electronic properties of a large set of synthetic chlorins, including insights into the origins of the spectral characteristics of a range of native chlorophyll chromophores (e.g., chlorophylls *a*,*b*,*d* and their pheophytin analogs). Overall, these studies advance our understanding of the photophysical properties and electronic structure of native photosynthetic chromophores and synthetic analogs for solar energy research.

A Concerted Synthetic, Spectroscopic, and Computational Approach towards Water Splitting by Heterometallic Complexes in Solution and on Surfaces

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Funding:	$440,000

PROGRAM SCOPE

The basic premise of our collaboration is to investigate the development of heterometallic complexes in solution and on surfaces aiming to interrogate the requirements necessary to integrating an antenna module, an active center module, and acceptor modules into a single molecule. The modular antenna is aimed to function as a sensitizer absorbing solar radiation and generating an excited state that can transfer an electron to the acceptor modules, as well as a hole to the active site module. The modular active site is required to acts as a donor, thus implying that the metal center will be able to reach a high-valent oxidation state that enables water oxidation.

Aiming to use Earth-abundant metals, we have been focusing our efforts toward cobalt-containing acceptors and manganese-containing active sites attached to antenna modules based on ruthenium polypiridine systems. 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 dioxygen and protons from water.

FY 2012 HIGHLIGHTS

Efforts made during FY 2012 include the study of (1) monometallic high-spin manganese(III) active sites, namely, the hexacoordinate [$Mn^{III}L^1$MeOH] and the pentacoordinate [$Mn^{III}L^2$] with asymmetric [N_2O_3] ligands, where the former can reach the needed high oxidation states for catalysis; (2) phenolate- and oxime-based monometallic low-spin cobalt(III) acceptors; and (3) the efficiencies of excited state electron transfer on ruthenium(II) antenna modules.

Ultra-Stable Molecule-Surface Architectures at Metal Oxides: Structure, Bonding, and Electron-Transfer Processes

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Funding:	$100,000

PROGRAM SCOPE

Metal oxides such as WO_3, Fe_2O_3, ZnO, and SnO_2 are useful because of their ability to facilitate charge separation and charge transfer. By forming junctions between two oxide materials, a built-in electric field is created that greatly facilitates the separation of charge. We are investigating the use of chemical assembly methods to form and characterize the electron-transfer properties of adducts between different oxide materials (such as Fe_2O_3-WO_3 "dyadic" structures) and between light-harvesting molecules and metal oxides. Of particular interest is the use of "click" chemistry to form photoelectrochemically active oxide-oxide junctions and to link light-harvesting molecules to SnO_2. SnO_2 and ZnO are of particular interest because these materials have electron mobilities several orders of magnitude faster than more commonly used oxides, and both can be grown as highly crystalline nanorods. Time-resolved surface photovoltage spectroscopy and time-resolved photoluminescence are being used to probe the charge transfer on time scales from microseconds to nanoseconds.

FY 2012 HIGHLIGHTS

We successfully developed and implemented the Cu(I)-catalyzed Azide-Alkyne Cycloaddition (CuAAC) reaction as a general route to forming charge-transferring interfaces between different oxide-based materials, including SnO_2, WO3, Fe_2O_3, and ZrO_2. We demonstrated that functionalization of one oxide with azide groups and a second azide with alkyne groups enabled “click” chemistry to be used to form nanoparticle-nanoparticle dyadic structures. Time-resolved surface photovoltage measurements showed that the nanoparticle dyadic structures provided enhanced charge-transfer efficiency. Complementary measurements of the photocatalytic efficiency were performed using methylene blue as a model system; the results demonstrated that the nanoparticle adducts had catalytic efficiency that was higher than either component alone, proving that interfacial band offset associated with the nanoparticle-nanoparticle heterojunction facilitates irreversible charge separation and enhanced photocatalytic efficiency. Finally, we demonstrated a new form of heteroleptic charge-transferring coordination complex on ZnO nanorods using a “bottoms-up” assembly technique in which the charge-transferring complex is directly assembled on the nanorod surface. We found that the bipyridylthione ligands provide strong binding of bipyridyl complexes directly to ZnO surfaces; exposure of the surface-bound complex to a $Ru(bpy)_2Cl_2$ complex in solution yielded a surface-bound $Ru(bpy)_3$ complex that exhibited good electron-injection characteristics on ZnO nanorods. This represents a new and general method for the “on-surface” assembly of light-harvesting molecules on surfaces.

A Combinatorial Approach to Realization of Efficient Water Photoelectrolysis

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Funding:	$120,000

PROGRAM SCOPE

The “Achilles Heel” of solar energy is that over 70% of current energy use is in the form of fuels. Photovoltaic cells that operate only during daylight hours can produce valuable electrical power but do not directly produce stored energy. Hydrogen obtained from renewable energy will be the fuel of choice either when fossil fuels become depleted or when the environmental consequences of burning fossil fuels are no longer acceptable. Direct photoelectrolysis of water using solar energy is the ideal method for producing hydrogen from a renewable, inexpensive and abundant raw material.

Due mainly to their inherent stability, semiconducting oxides are the strongest candidate materials to efficiently photoelectrolyze water. Due to the fact that no known oxides can efficiently and cheaply photoelectrolyze water, we have initiated a combinatorial approach to discover new oxide semiconductors.

FY 2012 HIGHLIGHTS

During the last year, we have been concerned with extending our combinatorial approach for preparing and screening oxide semiconductors to the optimization of materials that are known to have some photoelectrolysis activity. We have employed some unspent start-up funds to obtain an additional Fuji-Dimatix research grade ink jet printer. The additional printer was necessary to both increase our through put and to ensure that when a printer breaks down, as it did during a period in 2011, that we will be able to continue our research uninterrupted.

New printing templates have been designed, including a quaternary printing template designed by stacking Z-dimension slices of a 4-element tetrahedron. We have also begun to explore new compositions in both discovery and optimization modes. Theoretical work, inspired by our previous discovery of the CoAlFe oxide spinel system, determined that substitution of In and/or Ga for aluminum in the structure may both lower the band gap and increase the carrier mobility in the system. We have also begun to explore Cu containing oxides of Nb and Ta as a result of some work coming out of the Maggard lab at North Carolina State University. These phases can have low band gaps and optical transitions that appear to be direct.

Studies of Photoinduced Electron Transfer from Dyes, Polymers and Quantum Confined Systems into Semiconducting Single Crystals

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Funding:	$185,000

PROGRAM SCOPE

We conduct fundamental studies of the sensitization of single crystal large band gap semiconductors with a variety of different sensitizers that can extend the response of a photoconversion system into the visible region of the solar spectrum. Single crystal semiconductor electrodes are valuable model systems for elucidating the fundamental surface chemistry and electron transfer process important for the eventual implementation of solar energy converting devices. Over the last 18 years, we have developed techniques to make the semiconductor surface chemistry reproducible by either cleaving the semiconductor to produce clean new surfaces (SnS_2) or by polishing, etching, and photoelectrochemically treating to produce terraced surfaces and to remove surface contamination (anatase and rutile).

FY 2012 HIGHLIGHTS

In a series of publications, we first explored the surface chemistry of the QDs and their attachment to single crystal oxide semiconductor surfaces. For CdSe QDs, it was found that complete ligand exchange of the surfactant molecules, used in the synthesis, for shorter chain bifunctional surface capping groups, such as mercaptopropioic acid (MPA), was required in order to get reproducible attachment of the QDs to the semiconductor surface. We then moved on to try and stabilize the CdSe QDs to the presence of iodide/triiodide, often used as a regenerator in sensitized solar cells. It was found that type-I CdSe/ZnS core-shell QDs can effectively sensitize single crystal TiO_2 electrodes and continue to operate in a regenerative mode in an aerated iodide electrolyte for more than 20 hours. Core CdSe QDs degrade rapidly in the same electrolyte presumably due to CdI_2 formation. The possibility of exploring new core/shell nanomaterials in a variety of electrolyte/mediator combinations may result in more efficient and stable QD-SSCs.

Multiple exciton generation, the creation of two electron hole pairs from one high-energy photon, is well established in bulk semiconductors, but assessments of the efficiency of this effect remain controversial in quantum confined systems like semiconductor nanocrystals. We used a photoelectrochemical system composed of PbS nanocrystals chemically bound to TiO_2 single crystals to demonstrate the collection of photocurrents with quantum yields greater than one electron per photon. The strong electronic coupling and favorable energy level alignment between PbS nanocrystals and bulk TiO_2 facilitate extraction of multiple excitons more quickly than they recombine, as well as collection of hot electrons from higher QD states. Our results have implications for increasing the efficiency of photovoltaic devices by avoiding losses due to the thermalization of photogenerated carriers.

Oxomanganese Catalysts for Solar Fuel Production

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Funding:	$580,000

PROGRAM SCOPE

The design principles for efficient heterogeneous photocatalysis remain unclear and are the focus of this project. High-valent oxomanganese complexes have been studied in great detail to understand how Nature makes O_2 from water during photosynthesis. Sensitized titanium dioxide nanoparticles (NPs) are robust materials for efficient light harvesting by photoexcitation of surface complexes and interfacial electron transfer (IET). The goals of this project are to integrate these two systems to construct solar-driven photocatalytic cells, based on our own water-oxidation catalysts, and to investigate how to achieve the efficiency breakthroughs necessary to make photocatalytic water oxidation an economically viable solar fuel resource. Four research groups in the Chemistry Department at Yale University are working together to (1) synthesize titanium dioxide NPs and anchor-linker-ligand conjugates, (2) develop new methods for surface attachment of catalysts using oxidation-resistant anchors and linkers that are stable in water, (3) develop and apply computational methods to analyze IET and characterize catalytic water-oxidation complexes, and (4) use spectroscopic methods to characterize the photochemistry.

FY 2012 HIGHLIGHTS

We have explored design principles of molecular linkers for rectification of IET. A specific pair of molecular linkers, related by inversion of the direction of an amide bond connecting a photosensitizer to a catalyst, was found in which one of the linkers shows rectification while the other one does not. EPR and THz spectroscopic measurements and computational modeling of current-voltage characteristics confirm the asymmetry of electron transfer in these systems. We have also studied IET in polyoxotitanate nanoclusters derivatized on the surface with a molecular adsorbate (in collaboration with Philip Coppens and Jason Benedict, University of Buffalo). This work is the most comprehensive study to date of a sensitized semiconductor NP in which the structure of the surface and the mode of molecular adsorption are precisely defined by x-ray crystallography. In addition, we have synthesized a series of high-potential fluorinated porphyrins for use as photosensitizers for water oxidation at photoanodes in photoelectrochemical water-splitting cells. THz spectroscopic studies show the photoexcited dyes are capable of injecting electrons into the conduction band of titanium or tin dioxide. The reduction potentials of the resulting photogenerated porphyrin radical cations range from 1.35-1.65 V vs NHE, as reflected by the ability of dye-sensitized solar cells to use the Br_3^-/Br^- redox couple as a mediator with superior performance in comparison to results obtained using the lower potential I_3^-/I^- mediator. Computational modeling of the structures and equivalent circuits assists in a molecular-based understanding of these systems.

DOE National Laboratories

Hierarchical Photosynthetic Systems

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Funding:	$1,880,000

PROGRAM SCOPE

This program investigates fundamental mechanisms for coupling photons to fuels in hierarchical, biomimetic photosynthetic assemblies, and develops strategies for the design of sustainable photosynthetic systems for solar energy conversion. The program investigates photochemistry in natural and artificial photosynthetic assemblies as a means to resolve fundamental mechanisms for solar energy conversion, and uses this information (1) for the design of modular, biomimetic artificial photosynthetic architectures that implement design principles found in Nature and (2) to develop novel photosynthetic bio-hybrid approaches for achieving improved solar photons-to-fuels efficiency in photosynthesis by augmenting photosynthetic architectures with abiotic cofactors to achieve novel photocatalytic function. A distinguishing feature of this program is the combined use of advanced, 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 2012 HIGHLIGHTS

Highlights this year included the creation of self-assembling photosystem I-cobaloxime hydrogen producing catalyst hybrid that efficiently couples hydrogen production to photosynthetic light-induced electron transfer. This work is establishing a strategy for improving on the fundamental solar fuels efficiency of photosynthesis. Ultrafast transient optical spectroscopy analyses on photosynthetic reaction center single crystals revealed a remarkable, multiple-cofactor, delocalized character of the first light-created excited-states in reaction center photosynthesis. This work sheds light on Nature's nanoscale control of excited states, and suggests principles for the design of artificial photosynthetic systems. High energy x-ray scattering and atomic pair distribution function analyses determined the structure of the cobalt-phosphate amorphous film water-splitting catalyst used in artificial leaf devices. This work established a new approach to resolve mechanism for water-splitting and the design of advanced catalysts. Pump-probe, time-resolved synchrotron x-ray spectroscopy techniques were used to characterize the excited-state structure of a diruthenium chromophore. This work demonstrates the opportunity to use time-resolved x-ray techniques to follow excited-state atomic reorganization linked to solar energy conversion. High resolution electronic structure was determined using multi-frequency EPR and density functional theory. This work provides detail information on catalyst electronic structures required for the design of optimized solar fuels catalysis.

Catalyzed Water Oxidation by Solar Irradiation of Band-Gap-Narrowed Semiconductors

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Funding:	$800,000

PROGRAM SCOPE

We continue to attack four major issues hindering progress in solar-driven water splitting using an integrated experimental and theoretical approach that offers fundamental insights into the underlying photoelectrolysis processes occurring in band-gap-narrowed semiconductor and catalyst components. First, we are tuning known photostable semiconductors to control their light-harvesting and charge-separation abilities in order to achieve a better understanding of their structural and electronic properties, and, in addition, designing and characterizing new classes of visible-light photoactive semiconductors. Second, we are developing viable catalysts for the difficult four-electron water oxidation process by exploring the catalytic activity and mechanisms of molecular transition-metal complexes. Third, we are immobilizing the homogenous catalysts and metal oxide catalysts on electrodes and/or metal-oxide nanoparticles in order to determine the kinetics of electrochemical water oxidation in the absence of mass transport limitations, and identifying the intermediates by spectroscopic techniques. Finally, we are exploring the interfacial water-decomposition reactions that occur at bare and catalyst-functionalized semiconductor surfaces using carriers generated by visible-light irradiation with the goal of understanding semiconductor→catalyst→water charge transport. While many groups have reported measurable water-splitting activities, the breakthroughs needed to support a hydrogen economy will require integrated expertise in the co-dependent areas of semiconductor and catalyst development.

FY 2012 HIGHLIGHTS

A detailed characterization of intermediates in water oxidation catalyzed by a mononuclear Ru complex $[Ru^{II}–OH_2]^{2+}$ (Ru = Ru complex with one 4-*t*-butyl-2,6-di-1',8'-(naphthyrid-2'-yl)-pyridine ligand and two 4-picoline ligands) has been carried out using electrochemistry, UV-vis and resonance Raman spectroscopy, pulse radiolysis, stopped flow, and ESI-MS with $H_2{}^{18}O$ labeling experiments, and theoretical calculations. The most intriguing result reveals a new low-energy pathway: the formation of $[Ru^{III}–OOH]^{2+}$ proceeding via formation of $[Ru^{IV}=O]^{2+}$ followed by nucleophilic attack by a water molecule with the concomitant removal of an electron and a proton (“direct pathway”) at pH > 3.

The importance of pendent bases in promoting proton-coupled electron-transfer (PCET) reactions with low activation barriers has been discussed for H^+ reduction or H_2 oxidation by many groups. PCET is also essential for the $4e^-$ oxidation of water in order to mitigate charge buildup and to reduce overpotential. We investigated the redox and spectroscopic properties with geometric isomers of Ru complexes with pendent bases. While the proximal isomer that has an N-base in the second-coordination sphere shows catalytic activity toward proton reduction, but not toward water oxidation, the distal isomer exhibits the opposite behavior.

Physical Chemistry of Reaction Dynamics in Ionic Liquids

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Funding:	$150,000

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. The work performed at BNL focuses on pulse radiolysis and flash photolysis studies of diffusion and electron transfer phenomena in ionic liquids, including the use of pressure dependence to elucidate anomalous diffusion mechanisms and the details of solvation dynamics. The effects of local ionic liquid composition and structure on the energetics and dynamics of charge transfer is a particular focus.

FY 2012 HIGHLIGHTS

To explore the effects of charge type on electron transfer reactions in ILs, we used pulse radiolysis at the BNL LEAF picosecond pulse radiolysis facility to produce solvated electrons in an ionic liquid (C_4mpyrr NTf_2). The electrons were then captured by selected quasi-isostructural biaryl scavengers (biphenyl, *N*-phenylpyridinium cation and methylviologen dication). The resulting biaryl radical electron adducts have charges of -1, 0, and +1, respectively. We measured the rate constants for the reactions of these biaryl radicals with a series of methyl-substituted *p*-benzoquinones, including temperature dependences for selected reactant pairs, and we are presently extending the driving force range using halogenated benzoquinones in order to better estimate activationless electron transfer rate constants (k_{max}) for each biaryl radical species according to Marcus theory. We observe that the rate constants obtained for the reactions of neutral *N*-phenylpyridinyl radical at low driving force are similar to those of biphenyl radical anion at much higher driving force, indicating faster diffusion for the neutral species. Our kinetic results also clearly show that diffusion rates of solvated electrons in the ionic liquid are more like those of molecular anions than of quantum particles.

Reactive Intermediates in Condensed Phase: Radiation and Photochemistry

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Funding:	$540,000

PROGRAM SCOPE

The goal of this program is to study and gain an understanding of the fundamental processes associated with the interaction of ionizing radiation within bulk liquids, the liquid/solid, and solid/solid interface. Specific emphasis is placed upon developing detailed knowledge of the role of the solvent, the interface, and nano-confinement on charge recombination, electron transfer, energy transfer, and ion-radical chemistry. The processes that control these reactions, such as excited state chemistry, thermalization, solvation, and energy transfer, are among the most fundamental events that occur in condensed phase chemistry and the related areas of energy sciences, physics, and biology. While much is now understood about radiation chemistry in bulk liquids, there is still a significant gap in our knowledge of the many fundamental processes that lead to radiation damage. This is particularly true for the radiation chemistry of nanoconfined and interfacial systems. Detailed mechanisms for these processes are not known, and it is commonly accepted that these (and many other) radiation-induced processes involve exotic chemistry that occurs on an ultrafast timescale ($<10^{-10}$ s).

FY 2012 HIGHLIGHTS

The photochemistry of the charge transfer (CT) band of the room-temperature ionic liquid (RTIL) 1-hexyl-3-methylimidazolium bromide ($[\text{hmim}^+][\text{Br}^-]$) has been investigated using near-IR to Vis ultrafast transient absorption (TA) and steady-state UV absorption spectroscopies. Continuous irradiation of the CT band at 266 nm results in the production of photoproducts that absorb strongly at 266 nm. We have shown that these photoproducts, which are apparently very stable, adversely affect ultrafast TA measurements. Elimination of these effects reveals at least two transient species that exist within the TA detection window of 150 fs to 3 ns and 500 nm to 1250 nm. Initial interpretation of the data indicates the initial CT process results in complex reactions involving radical species and possibly the generation of reactive excited states.

We have studied the radiation chemistry water confined in porous silica (1-nm and 57-nm pore sizes) and compared these results to bulk water. The pulse radiolysis technique was used to investigate the evolution of the hydrated electron formed in water trapped in silica with 2 ns time resolution. Within the signal-to-noise of our experiment, the spectrum of the solvated electron is the same in both the bulk and confined media, indicating that within 20 ns, the electron solvates in the region of the pore that has bulk like properties and not at the interface. It is also observed that the reaction rates of the solvated electron increase with decreasing pore size and that the yield of the solvated electron increases with decreasing pore size.

Solar Fuel Production Catalyzed by Transition-Metal Complexes

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Funding:	$743,000

PROGRAM SCOPE

We are pursuing photoinduced catalytic reduction of CO_2 to CO and/or formate, and ultimately to methanol following the concept of coupled proton and hydride-ion transfer reactions. Methanol is the target fuel because it is easily transported and can be used in fuel cells of the future. We are exploring fundamental studies of the thermodynamic, kinetic, and photophysical and photochemical properties of M-H, M-C_1 metal complexes with an NADH model ligand, and bifunctional catalysts containing photoactive d^6 metal centers. Central to our strategy is the ability to investigate selected scenarios computationally in order to narrow the search for viable catalysts and processes. By manipulating a suitable choice of metals and ligands, coordination geometry, irradiation, oxidation state of the metal, and solvent (including $scCO_2$), we are carrying out reduction of CO_2 and its C_1 reduction products using ionic hydrogenation reactions that we are probing with unique tools (such as time-resolved IR and UV-vis and pulse radiolysis) in a strong collaboration between experiment and theory. Success in the research proposed here will provide an exciting avenue to solar fuel production from CO_2.

FY 2012 HIGHLIGHTS

Two geometric isomers of a ruthenium complex with a bio-inspired nicotinamide functionality can serve as precursors for the photo-generation of C–H hydrides for studying reactions pertinent to the photochemical reduction of metal–C_1 complexes and/or carbon dioxide. We found that a steric effect is important for proton, net-hydrogen-atom, and net-hydride transfer reactions.

We have investigated, through DFT calculations, the hydride donating power, or *hydricity*, of various ruthenium- and rhenium-based complexes that have the NADPH-model functions. These visible-light-generated complexes may be valuable for use in reducing CO_2 to fuels such as methanol via hydride transfer. Calculations indicate that a triply-reduced, doubly-protonated ruthenium complex, which could be experimentaly produced by a photochemical reaction, is sufficiently “hydridic” to reduce a metal-bound carbonyl on $CpRe(NO)(CO)_2$.

The mechanism of CO_2 reduction to CO and $HCOO^-$ mediated by $Re(bpy)(CO)_3X$ catalysts is poorly understood. We investigated the mechanism for CO production using density functional theory. Our previous experimental work with a simplified reaction mixture—one that removes the photo-reduction step—was used for validation of the proposed mechanism, which involves formation of a rhenium carboxylate dimer, $[Re(bpy)(CO)_3]_2(OCO)$.

Thermal, Photo and Radiation Induced Reactions in Condensed Media

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Funding:	$3,570,000

PROGRAM SCOPE

Using the complementary techniques of excitation by photons or fast electrons, we investigate the fundamental chemistry of solar energy conversion and chemistry initiated by ionizing radiation. The program combines powerful experimental techniques with computation and theory. A principal effort has been to develop advanced detection techniques, such as optical fiber single-shot detection and mid-IR detection, which enhance the unique capabilities of LEAF. Research in this program includes (1) quantitative determination of fast "step" processes for attachment of electrons and holes to conjugated polymers, (2) observation of charge transport over long distances along conjugated polymer chains, (3) fundamental radiation chemistry and electron transfer processes in ionic liquids, (4) reactivity pathways for nitrogen-containing radicals, (5) resolving major controversy about H atom reactivity toward tert-butanol, (6) insight into proton-coupled electron-transfer and hydride-transfer reactions in water or organic solvents, (7) binding of small molecules to metal complexes, (8) investigation of CO_2 photoreduction catalysts in supercritical CO_2 ($scCO_2$) and biphasic ionic liquid/$scCO_2$ solvents, (9) IR detection for clear identification of intermediates produced by photochemistry or ionizing radiation, and (10) utilization of accelerator and photochemical experimental facilities by many users and collaborators.

FY 2012 HIGHLIGHTS

A novel catalyst converts CO_2 and H_2 to formic acid storing energy, achieving the first reversible and recyclable H_2 storage under mild conditions. This energy-efficient and green system produces high-pressure CO-free H_2 in water and controls H_2 production or consumption using phi.

Spectroscopic results illuminate the nature of electrons in conjugated chains, confirming their polaron nature, showing that bipolarons are disfavored and showing that mixed polaron/bipolaron states exist.

Unprecedented measurements find large yields of hole capture in less than 15 ps, which may enable measures of rapid hole transport in conjugated polymers.

The temperature and viscosity dependences of photoinduced charge-separation reactions of a donor-bridge-acceptor system ionic liquids (IL) had a broad distribution of lifetimes, revealing the complexity of simple reactions in IL systems and effects of overlapping dynamical and ET time scales.

A new beam line coupled to a unique time-resolved infrared detection system at LEAF opens up new opportunities for the identification of short-lived radiation-induced intermediates, relevant solar energy conversion, catalysis, and chemistry associated with nuclear reactors.

Chemistry with Near Infrared Photons

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Funding:	$491,000

PROGRAM SCOPE

The purpose of the project is to develop robust inorganic light absorbers and catalysts for the synthesis of fuels and chemicals from carbon dioxide and water using sunlight as energy source. Our approach is to assemble all-inorganic molecularly defined units that serve as visible light charge transfer chromophores on nanopore silica surfaces coupled to multielectron catalysts for demanding redox reactions. Synthetic methods are being developed for making heterobinuclear transition metal chromophores, assembling catalyst clusters, and exploring core-shell geometries that afford coupling of the components across a proton transmitting nanoscale silica layer for separation of the water oxidation catalysis from all other photosynthetic processes. Structural characterization of components and assemblies by optical and vibrational spectroscopy, EXAFS analysis, XRD measurements, and high resolution TEM imaging play a key role in this effort. Elementary photocatalytic reaction steps of water oxidation and carbon dioxide reduction are monitored by time-resolved FT-IR spectroscopy. The mechanistic understanding gained from these studies, combined with electron transfer investigations of the heterobinuclear charge transfer units by transient optical spectroscopy, guide the design of units for improved photocatalytic efficiency under visible and near infrared light. The main long-term goal of the project is to close the complete photosynthetic cycle in a nanoscale core-shell construct with high selectivity under minimal loss of energy or charge.

FY 2012 HIGHLIGHTS

A spherical Co oxide (Co3O4)-silica core-shell nanostructure with organic molecular wires embedded in the silica layer and covalently attached to the Co oxide surface was developed. Efficient charge transport from a visible light sensitizer on the outside of the silica shell to the Co3O4 particle on the inside was demonstrated by direct monitoring of the hole by transient absorption spectroscopy. The constructs affords the separation of the water oxidation catalyst (Co3O4) from the light absorber and reductive chemistry.

Chemical intermediates of the water oxidation cycle on the catalyst surface of Ir oxide and Co oxide nanoparticles were directly observed for the first time using rapid scan FT-IR spectroscopy. Novel ZrOCo heterobinuclear units on the silica surface that afford reduction of carbon dioxide to carbon monoxide and formate with visible light were developed. Excited state lifetime and electron transfer studies of heterobinuclear units on silica nanopore surfaces in controlled environments (gas, liquid, vacuum) were accomplished by developing optically transparent (non-scattering) mesoporous silica films. Excited state lifetimes as long as a few microseconds were observed (room temperature). These samples open up detailed characterization of the electron transfer processes of the all-inorganic heterobinuclear units in controlled environments.

Primary Processes in Photosynthesis

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Funding:	$575,000

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 nature's supreme and most elegant examples of nanoscale engineering. 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 2012 HIGHLIGHTS

The bacterial reaction center (bRC) is a model photosynthetic system for studying the processes that convert light into charge separated species. Carotenoids and chlorophylls are close spatial neighbors in the bRC but have vastly different spectral absorption spectra. To investigate the energy transfer pathways between these pigments, we performed two-color 2D electronic spectroscopy (2D-ES) measurements exciting the S_2 state of the carotenoid at 500 nm and probing the Q_y band of bacteriochlorophyll *a* (BChl*a*) at 800 nm. These data revealed two competing energy transfer pathways between the carotenoid and BChl*a*. The dominant route was determined to proceed via internal conversion within the carotenoid to the S_1 state prior to energy transfer to the Q_y band of BChl*a*. This competition of energy transfer pathways, however, reveals a redundancy of effective routes that may play a role in photoprotection, i.e., providing an additional pathway for energy to pass to the carotenoid T_1 state.

One-color 2D-ES measurements were performed on the B band (800 nm) of the bRC to investigate the role of asymmetry in this pseudo-C_{2V} system. It is believed that the each of the two near identical branches of bRC performs the role of charge-separation or energy transfer. These 2D-ES spectra revealed, via use of cross-peak-specific polarization, energy transfer between the two states associated with the B band in under 100 fs. This equilibration between the two branches ensures that excitations do not get trapped within local minima of the branches when the reaction center is oxidized. Complimentary two-color coherence photon echo experiments between the BChl*a* (800 nm) and bacteriopheophytin *a* (BPhe*a*) (750 nm) pigments of the bRC show beating signals that persist for up to 2 ps. Further experiments and theoretical work is essential to understanding the origins of these oscillations, and if indeed they play a role in effective energy transfer within the bRC.

Coherence-specific polarization pulse sequences were used to isolate excitonic features that have hitherto been obscured in 2D-ES spectra. Experiments on LHCII revealed long-lived coherence between chlorophyll pigments that decay with two time constants: 47 fs and ~800 fs. Complimentary theoretical calculations showed that these timescales originate from weakly and moderately strongly coupled pigments.

Photochemical and Photoelectrochemical Conversion of Solar Energy and Novel Nanoscience, Thrust 1: Excitons in Molecular and Nanoscale Organic Systems

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Students:	3 Postdoctoral Fellow(s), 3 Graduate(s), 0 Undergraduate(s)
Funding:	$1,015,000

PROGRAM SCOPE

This proposal 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 2012 HIGHLIGHTS

Using time-resolved microwave conductivity, we have measured yields of charge creation in conjugated polymer films containing substituted fullerene acceptors that were highly-diluted, well-dispersed, and had energy states that could be systematically varied in order to control the driving force for the conversion process. From these studies, two unexpected features were observed: the existence of an optimal driving force and a loss in conversion efficiency if this force was exceeded. These conclusions have broad implications for the design and understanding of excitonic photovoltaics, with the optimum yield of carriers dependent on the specific pairing of donor and acceptor. *Journal Of Physical Chemistry C*, *116*, 8916−8923.

We have collaborated with researchers at the University of Oklahoma to produce and characterize novel materials based on isotope-labeled single-walled carbon nanotubes (SWCNTs). We combined the advantages of highly enriched SWCNT samples separated by electronic structure and diameter with 13C labeling to enhance the sensitivity and spectral resolution in solid-state NMR spectroscopy of SWCNTs.

The unprecedented range of highly enriched, well-characterized 13C-labeled SWCNT samples allowed us to rigorously address the theoretically predicted dependence of 13C chemical shift on SWCNT diameter and electronic structure. Beyond the fundamental importance of understanding the intrinsic magnetic properties of SWCNTs, 13C-labeled SWCNTs with well-characterized electronic structure could enable the rational design of interfaces in organic photovoltaic composites, batteries, and other devices. *J. Am. Chem. Soc.* 2012, 134, 4850−4856.

Photochemical and Photoelectrochemical Conversion of Solar Energy and Novel Nanoscience, Thrust 2: Quantum Confined Nanocrystals and Nanostructures

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Students:	2 Postdoctoral Fellow(s), 3 Graduate(s), 0 Undergraduate(s)
Funding:	$1,215,000

PROGRAM SCOPE

This proposal 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 2012 HIGHLIGHTS

A team of researchers at NREL used an advanced spectroscopic technique that monitors spin dynamics on the femtosecond timescale to determine that the exciton (the bound electron-hole pair) does not expand and separate along the length of a CdSe-seeded CdS rod, as had been previously proposed. In fact, for larger sizes, strain due to the mismatch of the microscopic crystal structures at the CdSe/CdS interface causes the exciton to flatten perpendicular to the long axis of the nanocrystal. This knowledge can inform the design of nanostructured materials engineered for efficient charge separation and transport. *ACS Nano*, 2012, 6, 5498.

Semiconductor QDs are novel optoelectronic systems that allow for tailored optical and electrical properties. Control over their surface composition and structure is an ongoing challenge, which if solved, should lead to a broader impact of QDs in many technological areas. As made, PbSe QDs are enriched with Pb at their surfaces rendering the QDs n-doped. Post reacting the QDs with a specially designed Se-ligand renders the QDs more Se enriched. The Se-ligand reacts one-to-one with the OA ligand. The resulting QDs are more stable towards oxidation, and similar strategies could result in “doping” of QDs. *Nano Lett.* 2011, 11,4923-31.

Sharp exponential (Urbach) band tails were found to be involved in carrier transport as well as a deep trap state at 0.2 eV. Contrary to usual expectations, the energetic disorder that characterizes the carrier transport is more similar to bulk polycrystalline semiconductors than other nanocrystal systems measured previously with very sharp (~14meV) band tails. Most surprisingly, the characteristic energy of the bandtails is much smaller than the bandwidth of the first exciton energy as seen in optical absorption spectra of the arrays (~170 meV). This surprising result indicates that QD materials can potentially compete with bulk systems allowing for very high quasi-Fermi level separations and therefore open circuit voltages. *Phys. Rev. B* 86, 155313 (2012).

Photochemical and Photoelectrochemical Conversion of Solar Energy and Novel Nanoscience, Thrust 3: Interfacial Photochemistry and Catalysis

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Sr. Investigator(s):	Frank, Arthur, National Renewable Energy Laboratory Gregg, Brian, National Renewable Energy Laboratory Neale, Nathan, National Renewable Energy Laboratory Turner, John, National Renewable Energy Laboratory
Students:	2 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$1,770,000

PROGRAM SCOPE

This proposal 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 examining the roles of intentional or unintentional surfaces sites—such as defects, nanostructure, interfacial layers, and catalysts—on charge transport and transfer in photoelectrochemical subsystems, and developing mechano-chemistry to understand how to control reactivity far from equilibrium.

FY 2012 HIGHLIGHTS

Silicon, which already dominates the world photovoltaic industry with more than 10 GW produced annually, is a non-toxic and earth-abundant element with a promising band structure for solar photoconversion. Si-based water-splitting systems could therefore realize low-cost, easily manufactured, and sustainable solar H_2 fuel production. Recently, we demonstrated that the nanostructured Si surface can significantly improve 3 critical properties of Si for PEC H_2 production. Nanoporous black Si increases the H_2-producing photocurrent density by about 20%, reduces the overpotential needed for H_2 generation by more than 70 mV, and facilitates H_2 gas evolution. We showed that the mechanism for these improvements stems from the unique nanostructured Si surface, which provides (1) near-ideal anti-reflection that enables the absorption of most incident light and its conversion to photogenerated electrons and (2) extremely high surface area in direct contact with water that reduces the overpotential needed for the PEC hydrogen half-reaction. Application of these advances would significantly improve the solar H_2 conversion efficiency of an ideal tandem PEC system. *Energy & Environmental Science* 4(5), 1690-1694 (2011).

This study addresses a long-standing controversy about the electron-transport mechanism in porous metal oxide semiconductor films that are commonly used in dye-sensitized solar cells and related systems. We investigated, by temperature-dependent time-of-flight measurements, the influence of proton intercalation on the electron-transport properties of nanoporous TiO_2 films. These measurements revealed that increasing the water content in the electrolyte led to increased proton intercalation into the TiO_2 films, slower transport, and a dramatic change in the dependence of the thermal activation energy (E_a) of the electron diffusion coefficient on the photogenerated electron density in the films. Random walk simulations based on a microscopic model incorporating exponential conduction band tail (CBT) trap states combined with a proton-induced shallow trap level with a long residence time accounted for the observed effects of proton intercalation on E_a. Application of this model to the experimental results explains the conditions under which E_a dependence on the photoelectron density is consistent with multiple trapping in exponential CBT states and under which it appears at variance with this model. *Nano Letters* 12, 2112-2116 (2012).

Fundamental Investigations of Complex Oxides for Visible Light Photoactivity

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Funding:	$650,000

PROGRAM SCOPE

We propose a combined experimental and theoretical approach to the study of the properties of epitaxial films of ternary oxides with perovskite-like structures whose optical spectra is suited for visible light photochemistry. Target materials will include ferrites, mixed ferrite-chromites, and oxynitrides of titanates. Correlations between bulk structure and the optical and charge carrier properties will be examined theoretically and manipulated experimentally using variations in stoichiometry and doping. Because surfaces and interfaces are the gateways through which solar chemical conversions take place, we will address how surface structure, both electronic and physical, affects charge transfer chemistry of adsorbates sensitive to electron transfer events to/from visible light generated charge carriers.

FY 2012 HIGHLIGHTS

We have begun surface chemistry studies of $LaFeO_3$, which is a charge transfer insulator with an optical band gap of ~2.2 eV and demonstrated visible light activity for degradation of various organic dyes, starting with photoemission studies of a commercially available powder that possessed an average 10 nm particle size. Heating the powder in vacuum at 400°C resulted in the appearance of a very weak Fe^{2+} feature on the high binding energy side of the prominent Fe 2p Fe^{3+} feature, indicating that vacuum annealing initiated some surface reduction. However, changes in the surface stoichiometry resulting from vacuum reduction were much more apparent in the La 3d lineshape, which is ultrasensitive to changes in the coordination environment about the La cation. The surface stoichiometry was readily restored by mild oxidation (at ~100°C), which provides evidence that the entire particle was not reduced or phase separated. FTIR work has begun on the adsorption properties of water and CO_2 on this powder. CO_2 binds strongly as carbonates, but water is only weakly held with little or no hydroxyl formation.

These observations suggest that the powder may be preferentially terminated with layers of La oxide since La_2O_3 is known for forming very stable carbonates.

In a separate effort, we have explored growth of $LaFeO_3$ and $LaCrO_3$ single crystal films on suitable lattice match oxide templates (e.g., $SrTiO_3$(001)). To minimize defect creation, the films were deposited using molecular beam epitaxy (MBE), in which the incoming atom energies were very low (< ~0.1 eV). Core-level and valence-band XPS spectra measured for MBE-grown $LaCrO_3$/$SrTiO_3$(001) yielded band offsets and potential gradients within the $LaCrO_3$ sufficient to trigger an electronic reconstruction to alleviate a potential polarity mismatch at the interface. Yet, the film was insulating. Based on first principles calculations, we attribute this unexpected result to interfacial cation mixing combined with charge redistribution within the CrO_2 layers, enabled by low-lying d states within $LaCrO_3$, which suppresses an electronic reconstruction. The impact of this mixing on the optical properties of the films will be explored.

III. SCIENTIFIC USER FACILITIES DIVISION

Institutions Receiving Grants

The Physics of Gain Mechanisms in Self-Amplified Spontaneous Emission Free Electron Lasers

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Students:	2 Postdoctoral Fellow(s), 5 Graduate(s), 5 Undergraduate(s)
Funding:	$337,500

PROGRAM SCOPE

This project is concerned with new methods of ultra-fast photon production based on high brightness electron beams and associated measurement techniques. The major light source/accelerator development projects funded by this effort are next-generation short-period, high field cryogenic undulators; experimental investigations of inverse Compton scattering (ICS) light sources; inverse free-electron laser (FEL) accelerators for new light sources; a table-top all-optical FEL based on GV/m laser-driven dielectric accelerators; dielectric and plasma wakefield acceleration; and novel photoinjector electron source development. Advanced beam and FEL diagnostics work includes development of new coherent imaging techniques for very high brightness electron beam profile measurements, and next-generation FROG measurements for quantifying single-spike FEL performance.

FY 2012 HIGHLIGHTS

This program has met with considerable success. A novel, very high field, 9-mm period cryo-undulator based on praseodymium was built and tested experimentally at the SLAC NLCTA. ICS in the strongly nonlinear regime was measured, with third harmonic radiation observed at BNL. A photonic dielectric laser-driven accelerator has been developed, along with very high field electromagnetic undulators (tested at SLAC and BNL) in an initiative shared with DARPA. This effort is complemented by dielectic wakefield acceleration experiments; wakes in slab-symmetric structures typical of dielectric laser were observed at BNL. These experiments are being extended at the GV/m level at the SLAC FACET facility in SLAC experiment E-201. Another experiment at FACET was initiated in 2012—the so-called plasma photocathode experiment (E-210) that promises to produce a beam of unprecedented brightness, capable of driving an x-ray FEL. A new class of photoinjector has been introduced here—the hybrid standing/travelling wave device (fabricated and commissioned this year at UCLA) that produces ultra-short electron pulses. A revolutionary new beam diagnostic technique based on coherent imaging of transition radiation, using methods borrowed from the coherent x-ray FEL community, has been measured. On the FEL side, a new transient-grating FROG technique was used to measure sub-100 fs single-spike FEL pulses at the SPARC FEL (Frascati, Italy). These results have produced a dozen high profile publications (in PRL, APL, Phys. Plasmas, etc.) and aided in the graduation of three PhDs who are now contributing to the U.S. research effort in accelerator and light source sciences.

Versatile, Programmable Area Pixel Array Detector for Time-Resolved Synchrotron X-Ray Applications

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Philipp, Hugh, Cornell University

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Funding: $525,000

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 grant is to develop a programmable, silicon-based area detector that can directly address the needs of the scientific community by providing customized, programmable, real-time processing of data. The front-end detector hardware comprises a pixelated, high-resistivity, direct-detection, silicon diode that is connected at the pixel-level to a CMOS Application Specific Integrated Circuit (ASIC). The CMOS is fabricated by taking advantage of highly-refined, commercialized manufacturing processes. Each pixel of the detector being developed has circuitry for detecting single x-rays and signal conditioning. The pixels use a high-speed, low-level, semi-synchronous data interface to communicate with field programmable gate arrays (FPGAs). This low-level interface to programmable logic will make a hugely powerful and flexible tool available to the synchrotron radiation community.

Since the design and fabrication of custom, large-format ASICs suitable for area detectors are 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. Utilizing the past experiences of our detector development group, we have been (1) performing R&D on novel FPGA-reliant pixel designs, (2) adapting pixel circuits developed in the past to new FPGA controller hardware to realize usable detectors as rapidly as possible, and (3) implementing the resultant detectors for a wide variety of experimental applications at synchrotron radiation sources.

FY 2012 HIGHLIGHTS

With respect to the three points of approach in the previous paragraph, we have (1) designed and fabricated novel integrated circuits to test FPGA-reliant designs. These are now undergoing electronics testing. (2) We have designed and assembled a 256 x 384 pixel array detector based on a mixed-mode ASIC coupled to a high-speed FPGA interface. This detector has a wider dynamic range than any previous such device. (3) The mixed-mode detector has been tested at three synchrotron sources in time-resolved coherent diffraction imaging and materials science experiments. All three tests were successful and demonstrated the advantages of our approach. Results are being prepared for publication.

Key Laser Technologies for X-Ray Free-Electron Lasers

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Funding:	$367,500

PROGRAM SCOPE

Over the last few years, advances in femtosecond lasers have opened up the possibility of constructing fully coherent soft and hard x-ray sources via kilometer-long seeded EUV or x-ray Free-Electron Lasers (FELs). These facilities will be combined laser and accelerator laboratories. In this project, we develop some of the key laser technologies needed to make such facilities fully functional and to enable completely new research capabilities. In particular, we focus on a pulsed timing distribution and synchronization systems that will enable long term stable sub-femtosecond timing of lasers and microwave sources in kilometer scale FEL and accelerator facilities. To achieve such precise timing, we use the unique low jitter properties of femtosecond lasers and a new class of high sensitivity timing detectors based on nonlinear optics and sampling techniques rather than pure microwave techniques. Timing distribution test beds on the 1km length scale will be demonstrated at the sub-femtosecond and eventually sub-100 attosecond jitter level. Key technologies investigated are (1) fiber and solid-state lasers and their jitter evaluation to design and fabricate a suitable ultra-short pulse laser that can serve as an optical master oscillator for an advanced timing distribution system; (2) polarization maintaining and dispersion compensated fiber links; (3) integrated optical balanced cross-correlators; and (4) balanced optical microwave phase detectors for precision optical and microwave extraction and synchronization.

FY 2012 HIGHLIGHTS

In the second project year, we have confirmed the theoretical scaling of jitter in short pulse laser systems and demonstrated ultralow jitter measurements on the pulse streams from 10-fs Ti:Sapphire lasers, which can be synchronized to within 13 as confirmation that sub-100 timing distribution systems are possible using optical pulsed timing distribution systems, which appeared in Nature Photonics. Ultimately, such precision can only be supported long-term stable in an all-fiber system. Thus the second major highlight in year 2 of this project is the demonstration of the first dispersion compensated fiber link over 1.2 km distance in collaboration with OFS Laboratories. The link maintained timing within 2fs over 13 days of operation and 250as over 2 days of operation.

Optics for Advanced Neutron Imaging & Scattering

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Students:	1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$201,000

PROGRAM SCOPE

We are developing novel neutron focusing optics, which can be used to improve the performance of existing neutron scattering instruments and even lead to new instruments with unique capabilities. Collecting as many neutrons as possible is not the only motivation for using neutron focusing optics, albeit the most obvious. The relative weakness of neutron sources and slow incremental improvements of their strength means that the efficient use of existing sources can be as important a path toward more powerful instruments as the design of brighter sources. New tools for manipulating neutron beams might bring transformative improvements of neutron instrumentation and enable new science. We have demonstrated such a new tool: grazing-incidence mirrors based on full figures of revolution, known as Wolter optics. Axisymmetric mirrors are made by a replication technique developed for x-ray astronomy. This technology permits nesting coaxial mirrors and coating mirrors with multilayers possessing large critical reflection angle. Both nesting and coating lead to significant improvements in collection efficiency of the mirrors.

FY 2012 HIGHLIGHTS

We are developing mirrors for small-angle neutron scattering (SANS) and imaging instruments. Improvements of SANS instruments would have major impact on a large multidisciplinary community of users. Most existing SANS instruments achieve high resolution by collimating the beam by using small apertures, even though they severely constrain the neutron flux on the sample and thus the signal rate. Significant enhancements in both the signal rate and resolution are possible by using focusing optics. Our ray-tracing simulations of a SANS instrument equipped with Wolter optics predicted that the signal could increase by a factor of fifty or more, with the resolution improved by a factor of two. The optics can be optimized for SANS instruments at both pulsed and reactor sources, leading to major enhancements in their performance.

Imaging with thermal neutrons is an important method of examining materials and man-made objects, such as porous substances, fuel cells, car engines, and cultural heritage objects. Plans for the new neutron-imaging instrument at the Spallation Neutron Source attest to the growing importance of this technique. The goal of the imaging community is to achieve the spatial resolution of 1 micron, reaching the mesoscopic scale. Available detector resolution and neutron fluxes have so far prevented achieving this goal, but Wolter optics can be used to overcome these limitations. For example, with 10-fold magnification, the 1-micron-resolution goal is reachable using standard detectors with 10-micron pixels. Also, with the help of the optics, a much larger fraction of neutrons from the source could contribute to image formation. We have recently showed imaging with Wolter optics, demonstrating a neutron microscope with the magnification of four.

Picosecond X-Ray Detector for Synchrotrons

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Students:	0 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$107,467

PROGRAM SCOPE

The primary objective is to design, fabricate, and utilize a new x-ray detector for synchrotron studies of fundamental dynamics in complex materials on the picosecond ultrafast time scale. The proposed picosecond x-ray detector will substantially increase the capabilities of current synchrotron light sources by bringing pump-probe time resolution down from the ~100 ps bunch duration to the ~1 ps limit of semiconductor defect-limited carrier lifetimes, without needing to alter the synchrotron source radiation characteristics. The detector is a simple, coplanar stripline circuit on GaAs, where the electrical pulse generated by the synchrotron x-ray pulse is measured slice by slice using a sub-picosecond laser pulse. The essential step of reducing the GaAs carrier lifetime below one picosecond is achieved via energetic proton bombardment.

FY 2012 HIGHLIGHTS

The highlight of the year was the first successful measurement of the synchrotron pulse time profile with time resolution much less than the 80 ps FWHM duration of the Advanced Photon Source bunch length. This validates the fundamental premise of this research project, that time-resolved measurements at synchrotrons can break through the 80-100 ps pulse duration limit with this type of detector for pump-probe experiments. This experimental breakthrough first required the fabrication of a coplanar stripline circuit using Au electrodes on GaAs substrates. A circuit was designed that minimized pulse reflections at impedance jumps in the circuit and spread out these reflected pulses in time so that they could be separately resolved. When a prototype device on an as-delivered semi-insulating GaAs substrate was tested at the APS, using the synchronized laser pulses of APS Sector 7, a strong change in current versus x-ray/laser time delay was readily measured, giving the synchrotron pulse convoluted with the ~200 ps carrier lifetime in GaAs. The measurement was repeated with a new device that had been bombarded with 8 MeV protons using Purdue's van de Graaff accelerator (PRIME Lab) to create a uniform vacancy density throughout the depth reached by the 12 keV x-ray pulses. This measurement clearly resolved the primary x-ray pulse plus two other reflected pulses from the circuit, each with time resolution much better than the 80 ps FWHM APS pulse duration.

Photocathodes for High Repetition Rate Light Sources (partnership with LBNL, BNL-complementary R&D)

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Sr. Investigator(s):	
Students:	2 Postdoctoral Fellow(s), 2 Graduate(s), 1 Undergraduate(s)
Funding:	$333,000

PROGRAM SCOPE

This project brings together teams at Brookhaven National Laboratory, Lawrence Berkeley National Laboratory, and Stony Brook University to study photocathodes for high repetition rate light sources such as Free Electron Lasers and Energy Recovery Linacs, including testing RF photoguns, both normal-conducting and superconducting.

This R&D program leverages enormous assets at the three institutions. This work makes extensive use of synchrotron radiation materials science techniques, including powder and single crystal diffraction, x-ray fluorescence, EXAFS, ARPES, PEEM, and variable energy XPS. Use of these is a major thrust of our program and brings our understanding of these complex materials to a new level. SRF electron guns at Stony Brook University are being used for the study, and education of graduate students and post docs is an important aspect of our work.

FY 2012 HIGHLIGHTS

Preliminary results with the new assembled equipment has been obtained for providing cathodes for the two different guns under development: the 704 MHz and the 112 MHz systems. One chamber for each gun has been assembled and commissioned. Both systems have been tested and have produced the first cathodes.

The system for preparation cathodes for the 704 MHz gun consists of a main chamber with a number of ports to accommodate view ports, RGA, crystal monitor, anode, heating system, and the load-lock. In addition, three arms—one for each of the sources (Sb, K, and Cs)—are attached to it through gate valves. The sources can be inserted into the main chamber in front of the cathode using the manipulators holding the sources. The cathode stalk and the cathode substrate can be moved between the deposition chamber and the gun while maintaining UHV conditions in the vicinity of the substrate/cathode. This is done by the use of a load-lock system, a transport cart that contains the stalk, valves, vacuum equipment, and more. The transport cart is used to transfer the cathode between the deposition chamber and the gun. We prepared two transport carts that allow parallel processing of cathode growth and cathode insertion into the gun. The substrate can be heated or cooled by flowing gas through a pipe in contact with the substrate.

A new system has been built for cathode analysis in the light source, NSLS. At the same time, the system has been designed to provide cathodes to the 112 MHz gun. A load-lock system, which we call *vacuum-suitcase* for this gun, performs the Ultra High Vacuum transport of the cathode. The vacuum-suitcase has been designed and built and is under progress to be attached to the deposition chamber.

Construction and Test of a Novel Superconducting RF Electron Gun

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Fisher, Michael, Wisconsin-Madison, University of
Green, Michael, Wisconsin-Madison, University of
Rogers, Greg, Wisconsin-Madison, University of
Eisert, David, Wisconsin-Madison, University of
Bosch, Robert, Wisconsin-Madison, University of
Kleman, Kevin, Wisconsin-Madison, University of
Students: 0 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding: $1,125,000

PROGRAM SCOPE

The frontier of light-source-enabled science in the 21st century is where physical, chemical, and biological systems can be viewed on their characteristic temporal, spatial, and energy scales—femtoseconds, nanometers, and millivolts. Free electron lasers (FELs) are uniquely suited to achieving these goals, far exceeding the capabilities of other electron-beam technologies because of the inherent coherence of the FEL process.

Superconducting RF electron guns hold out the promise of very bright beams for use in electron injectors in CW free electron lasers, the next generation of FEL development. This program is to demonstrate a low frequency electron gun based on a quarter wave resonator (QWR) cavity. The goal for the UW gun is to achieve a peak field of 40 MV/m on the cathode in CW mode, factors of two or more higher that can be achieved with room temperature RF or DC technologies. The design flexibility offered also allows for the high exit energy of 4 MeV. This gun uses blow-out mode bunches in which a charge pancake is produced and allowed to expand under its own space charge into an elliptical bunch with constant charge density. This renders a potentially less modulated bunch for use in the FEL frequency up conversion process. The gun itself has been modeled with a 200 pC bunch to produce less than 1 micron normalized transverse emittance. The gun has also been modeled using 20 pC bunches for a lower emittance configuration. In that mode, simulations indicate a projected normalized transverse emittance of 0.3 mmmrad and an output slice energy spread of 0.6-0.8 keV.

FY 2012 HIGHLIGHTS

Major procurements have been completed, including the superconducting cavity, cryostat, photocathode laser, high temperature superconducting solenoid, beam transport, and high power and low level RF. The accelerator vault and clean room have been refurbished. Tests were completed at the cavity vendor Niowave, which show Q and gradient consistent with ultimate performance goals. Final assembly of the cryomodule and support systems are under way, with installation complete in March 2013. Beam tests will commence in April 2013, with beam characterization proceeding till the end of the grant.

DOE National Laboratories

Combining Scanning Probe Microscopy and Synchrotron Radiation for Nanoscale Imaging with Chemical, Electronic, and Magnetic Contrast

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Funding:	$500,000

PROGRAM SCOPE

The objective of this research is to develop a novel high-resolution microscopy technique for imaging of nanoscale materials with chemical, electronic, and magnetic contrast. It will combine the sub-nanometer spatial resolution of scanning probe microscopy with the chemical, electronic, and magnetic sensitivity of synchrotron radiation. The proposed 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 2012 HIGHLIGHTS

We have developed the conceptual design for a specialized scanning tunneling microscope that can be operated at cryogenic temperatures in ultra-high vacuum at synchrotron beamlines. Motorized stages for the alignment of the microscope in respect to the synchrotron beam (x, y, z, and rotation) have been designed that will provide the required stiffness and accuracy. Furthermore, we have integrated a flow cryostat into our current prototype microscope. In order to enhance the signal-to-noise ratio in our experiments, we have developed and utilized insulator-coated smart tips (tungsten and platin-iridium) with sub-micron conducting apex.

Advanced Detector Development for Synchrotron Radiation

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Principal Investigator:	Siddons, David
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Students:	0 Postdoctoral Fellow(s), 0 Graduate(s), 1 Undergraduate(s)
Funding:	$424,000

PROGRAM SCOPE

The project aims to develop two novel detectors:

(1) A detector aimed at the x-ray correlation spectroscopy experiment, which is currently extremely detector-limited. Our partners in this project are Fermilab and UGH Krakow. In previous years, we have invested money and effort into the project, contributing to foundry and bonding costs, and fabricating the silicon sensors in-house at BNL. We will keep our connection to this project by continuing to fabricate sensor wafers as required and providing readout electronics and real-time data analysis hardware. We will not, however, contribute fiscally to the Fermilab effort.

(2) An advanced x-ray imaging detector that can provide spectral as well as spatial information. The ASIC design and layout will be done by our colleagues in BNL's Instrumentation Division, funded primarily by laboratory overhead. We will fund ASIC fabrication from the project. We will use our in-house foundry and project-funded manpower to provide custom sensors to mate with the ASIC. The sensors will piggy-back on a wafer design intended to provide strip-detector arrays for our SBIR partners in another, unrelated, project. The sensors we need for this project are very small and can be accommodated easily in unused areas of that wafer. The lithography masks for that wafer are funded through the SBIR.

FY 2012 HIGHLIGHTS

Funding for the project was not received until August 2012, and so the results reflect a 2-month period, not a full year.

First tests of the 3D-integrated ASIC for the detector for speckle experiments (VIPIC) were successful. This is a major achievement. We believe this is the first successful detector project based on 3D-integration, and this raises significantly the prospects for further development of smart detectors. We look forward to beam tests in the coming months.

The schematic and floor plan of the ASIC for the energy-resolving imaging detector (HEXID) was completed and transistor-level layout is almost complete.

Experimental R&D Program at Brookhaven Accelerator Test Facility

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Students:	2 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$450,000

PROGRAM SCOPE

Featuring a high-brightness 80-MeV linac, a Terawatt picosecond CO_2 laser, and a variety of experimental tools (such as laser/e-beam interaction chambers, capillary plasma source, etc.), the Accelerator Test Facility (ATF) supports users’ research in advanced accelerators and radiation sources. The ongoing 26 experiments—12 active experiments, 4 completed experiments, and 10 new proposals—were reviewed at the Users' and Program Advisory Committee Meeting in April 2012.

FY 2012 HIGHLIGHTS

During FY 2012, 34 users (including 11 students) from 12 institutions set up and conducted their experiments at the ATF. Eleven ATF users' experiments received a total of 188 run-days. The experimental program at the ATF is evolving through introduction of new means for manipulating an electron beam, including (1) a mask technique for resonant plasma wakefield excitation and narrow band THz source with dielectric structures, (2) shaped drive and witness bunches combined with adjustable delay for precise mapping of the wakefield in dielectric structures and observation of beam self-modulation in plasma, (3) chirped beam with time-correlated energy distribution for the observation of CSR suppression with shielded plates, and (4) sub-5 micron beam development for miniature structure-based accelerators and radiation sources.

The 2012 experimental activity added a number of new scientific accomplishments. The main results are highlighted in the following 2012 PRL publications: "Experimental Observation of Energy Modulation in Electron Beams Passing through Terahertz Dielectric Wakefield Structures"; "Dielectric Wakefield Acceleration of a Relativistic Electron Beam in a Slab-Symmetric Dielectric Lined Waveguide"; "Experimental Study of Current Filamentation Instability"; "Experimental Observation of Suppression of Coherent-Synchrotron-Radiation–Induced Beam-Energy Spread with Shielding Plates"; "Experimental Demonstration of Wakefield Effects in a THz Planar Diamond Accelerating Structure"; and "Single Shot Diffraction of Picosecond 8.7 keV X-ray Pulses".

Two Ph.D. theses were completed based on the obtained experimental results.

In 2012, the ATF upgraded their picosecond CO_2 laser to support strong field experiments. Ti:Sapphire-based 10-μm OPA replaced an old picosecond CO_2 seed pulse generator. This will reduce seed pulse duration and increase seed energy. Combined with applying CPA method, this innovation should allow a ten-fold increase in the CO_2 laser peak power to about 10 TW.

Future plans include moving the facility to a more spacious building, thereby increasing the experiment floor space, allowing linac upgrade to higher energy (up to 500 MeV) as well as ATF CO_2 laser power upgrade.

Photocathodes for High Repetition Rate Light Sources (Partnership with Stony Brook University and LBNL)

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Students:	1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$335,000

PROGRAM SCOPE

The focus of this project is on photocathodes for high repetition rate Free Electron Lasers (FELs) and Energy Recovery Linacs (ERLs), including testing within RF photoguns, both normal-conducting and superconducting. Teams from LBNL, BNL, and Stony Brook University (SBU) lead this project and coordinate their efforts over a range of topics.

The program is concentrated in three areas: (1) physics and chemistry of alkali-antimonide cathodes (LBNL – BNL), (2) development and testing of a diamond amplifier for photocathodes (SBU - BNL), and (3) tests of both cathodes in superconducting RF photoguns (SBU) and copper RF photoguns (LBNL).

The work on alkali antimonides is focused on understanding the emission properties and growth of these materials in an effort to improve their performance. These materials have been made so far by an empirical design process, and our goal is to understand why certain methods work and some fail. Ultimately new materials will be fabricated with more optimum performance based on this work. This is expected to impact the design of a new generation of high repetition rate x-ray sources.

FY 2012 HIGHLIGHTS

We have been able to fabricate high Quantum Efficiency (QE) cathodes, yielding more than 6% QE in the green. We have measured the emittance of these cathodes using a lab-based technique, and obtained a value as low as 0.36 microns; this is significantly less than required for FEL operation. We have commissioned a new endstation vacuum chamber for NSLS beamline X21 for in-situ cathode studies. We have used the tools of synchrotron-based materials science (XRD) and lab-based tools (SEM, UHV-AFM and XPS) to understand the growth of the materials. For the first time, we now have an initial picture of how the reaction of K and Cs with Sb happens, what controls the kinetics, and what leads to reliable high performance cathodes. A significant challenge is that production by thermal reaction results in rough films. The consequence is increased emittance in a high-field environment; so we are investigating non-thermal means to make these materials.

Large Dynamic Range Beam Diagnostics and Beam Dynamics Studies for High Current Electron LINACs

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Sr. Investigator(s):	
Students:	0 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$500,000

PROGRAM SCOPE

The goals of this program are to develop new instruments for electron beam diagnostics and use these instruments for measurements of a beam 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 main 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 came from two directions.

(1) 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. It is envisioned to accomplish this using CW SRF LINACs and increasing the average beam current by many orders of magnitude. Such large increase in the average beam current and beam power a very small (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 we need to measure and take in to account fractions of the beam as small as 10^{-6}. This is a non-trivial task.

(2) There is an existing IR FEL facility—the Jefferson Lab FEL—that operated with the large average beam current. This facility provides excellent 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 2012 HIGHLIGHTS

We have been designing and building two different diagnostics for the transverse beam profile measurements with the LDR. The first one is a novel wire scanner with a detector working in counting mode, measuring visible photons generated via transition radiation. The second one is a beam viewer with a detection scheme comprised of two imaging sensors and an image intensifier. The designs are complete, necessary parts will be manufactured, and we will install these instruments on the accelerator shortly after that. We also have made beam measurements with existing beam viewers to test out LDR imaging paradigm. We have demonstrated imaging with dynamic range of 5×10^4, increasing the dynamic range by factor 10^2. We have used this setup to measure beam emittance and Twiss parameters. The measurements show that for a non-Gaussian LINAC beams, the dynamic range that is used can have dramatic impact on the measured beam parameters.

SRF Developments for Next Generation Light Sources

Institution:	Jefferson Lab
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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

We operate an R&D test facility to study the physics of 4th generation light sources. The BES funded activities are guided by developing user needs for 4th generation light sources, and also by the road-map defined by the BES sponsored Barletta-Corlett report [Nucl. Instr. & Methods A618 69 (2010)].

Our specific area of expertise is the development and operational experience with superconducting linac technology for next generation light sources, and the concomitant electron beam dynamics and photon production. We are investigating both high current and high gradient superconducting linacs that, unlike copper linacs, run with continuous wave radio frequency and, thus, produce a continuous stream of electron bunches at repetition rates of many MHz.

We have designed a high current linac optimized for light source applications, and have successfully installed and operated the world’s highest gradient CW superconducting linac. Using this linac, we studied the propagation of low emittance electron beams in our re-circulating, energy-recovering machine and FEL gain mechanisms. We used the setup to drive an oscillator-based UV-FEL with harmonics up to 10 eV at brightness levels 2 orders of magnitude higher than storage ring-based sources [Benson et al Nucl. Instr. & Methods A649 9 (2011)].

We are currently working on optical and physics designs for an oscillator-based free electron laser at up to 100 eV with harmonics stretching into the water-window region. Such a setup is within the capability of an upgrade to our existing facility [Benson et al, J. Mod. Optics 58 1438 (2011)].

FY 2012 HIGHLIGHTS

We were not funded in FY 2012, but we utilized Virginia and ONR funds to operate the R&D test facility to deliver 10 eV light to a user lab with a brightness higher than that obtained from storage rings. The user is an Argonne/ODU collaboration studying metastable Kr as part of an atom trap trace analysis project with the eventual aim of dating polar ice-caps [Jiang et al, Geochimica et Cosmochimica Acta 91 1 (2012)].

Superconducting Accelerator R&D for Coherent Light Sources

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

PROGRAM SCOPE

This program is based on development of a compact, cost-effective electron accelerator capable of producing 20 MeV electron beams of up to 1 mA. The accelerator development is part of a concept developed by MIT for utilizing Compton scattering to produce outstanding x-ray brilliance, well beyond that available from conventional sources. These x-rays are required for basic science and medical research. Affordable compact x-ray sources are required by universities and medical research labs. This accelerator design will operate at 4 Kelvin to minimize operating costs. An innovative superconducting material, Nb3Sn, is also being evaluated for additional energy-saving benefits.

FY 2012 HIGHLIGHTS

The Accelerator R&D for 2012 developed two superconducting accelerator cavity designs which were optimized for 4 Kelvin operations and low dynamic heat loads. One design was a two-spoke cavity, and the other was a three-cell elliptical cavity. The modeling consisted of electrodynamics, beam dynamics, and structural design which allowed for cavities performances to be compared. A cavity down select was made, and materials for fabrication were ordered. The low level RF test hardware was designed and fabricated along with the development of a test cryostat 3D model. Both the RF and the cryostat are necessary for evaluation of cavity performances.

Two successful test samples of Nb3Sn were produced, each showing transition temperatures of 18 Kelvin; the facility to apply this new material for superconducting cavities to further explore this exciting new material was designed; and procurement was started.

Additionally, plasma cleaning of niobium surfaces to minimize heat loads from surface contaminants was explored with an existing facility, and a full understanding of the operating range, gas pressure, and RF power was documented and will be further explored for application to the down selected cavity design.

Accelerator Research for a Next Generation Light Source (Development of a VHF Normal Conducting Photocathodes RF Electron Gun)

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Funding:	$898,000

PROGRAM SCOPE

This project is for the development of a high-brightness, high-repetition rate (MHz-class) electron injector for x-ray free electron laser (FEL) and other light source applications. The injector is based on a radio-frequency photocathode electron gun, taking the approach of utilizing a normal conducting cavity resonating in the VHF band at 186 MHz, operated in continuous wave (CW) mode. The gun incorporates high quantum efficiency (QE) photocathodes driven by a laser and capable of delivering the required charge at MHz repetition rates without significant demands on the drive laser technology. This approach uses technologies well proven in other applications and applies them in a unique combination that provides a highly robust and reliable system. Design features of the gun include a very high vacuum pumping capacity to allow use of high QE photocathode materials sensitive to contamination from residual vacuum components, and a load-lock for interchange of photocathodes of different materials in a controlled ultra-high vacuum system to prevent spoiling of delicate photo-emitting surfaces. We collaborate with teams at Cornell University, Argonne National Laboratory, and INFN-LASA (Milan, Italy) in diagnostics, linear accelerating structures, and photocathodes, incorporating and developing their designs to produce an integrated systems design that takes advantage of their best features. An existing shielded enclosure at the LBNL Advanced Light Source is used to house the experimental equipment. The project is staged in three phases: Phase-0 involves fabrication and test of the CW VHF gun to validate design features and performance of this most critical component in the injector, Phase-I tests photoemission from different photocathodes at the gun energy and at MHz repetition rate to validate the reliable production of electron bunches of high quality, and Phase-II adds beam manipulations, acceleration systems, and diagnostics to allow measurement of the 6-D brightness of the beam at a reduced repetition rate. These three phases allow full measurement of the injector performance in producing the required beam quality and repetition rate, in a cost-effective staged approach.

FY 2012 HIGHLIGHTS

The installation of the Phase-0 components and the commissioning of the VHF gun have been successfully completed, and the operation of the gun at design power and electric field levels demonstrated. The vacuum systems have been tested, and the excellent vacuum level in the gun is consistent with expectations. Measurements of dark current have been made, and initial measurements of photoemission from two types of photocathodes: in the first case, laser-induced emission from a bare molybdenum surface, and secondly, tests of a diamond amplifier photocathode in collaboration with a team from Brookhaven National Laboratory. These tests have demonstrated functionality of the gun and basic drive laser and diagnostics systems. Instrumentation and diagnostics components for Phase-I have been fabricated, and design and specification of components and layout for Phase-II developed. In the next period, completing Phase-I, we will proceed with characterization of electron beam emitted from semiconductor photocathodes in the gun, at MHz repetition rate.

Advanced Modeling of Accelerators for Next Generation Light Sources

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Students:	1 Postdoctoral Fellow(s), 0 Graduate(s), 1 Undergraduate(s)
Funding:	$272,641

PROGRAM SCOPE

This project is to develop an advanced modeling capability for electron accelerator beam delivery systems for next-generation light source applications. Building upon an existing parallel three-dimensional beam dynamics simulation package, the IMPACT code suite, we will develop new parallel, multi-scale methods for modeling phenomena in future light sources that cannot currently be modeled adequately. We will also advance the state-of-the-art in start-to-end, 3-dimensional, multi-physics modeling capabilities and will develop a simulation-based parallel optimization capability for accelerator design and operation. This work will lead to a high-resolution, 3-dimensional, multi-physics, advanced computational tool that will allow rapid design of coherent x-ray sources for optimal performance while minimizing technical risk and cost.

FY 2012 HIGHLIGHTS

Significant progress has been made in this project. We have integrated the injector, linac, and free electron laser (FEL) x-ray radiation simulation into a single code, *IMPACT*. We have carried out the first start-to-end simulation from the birth of the electron beam out of the photocathode to the production of coherent x-ray radiation in the undulator using the real number of electrons (~2 billions). This simulation faithfully captures the real shot noise inside the electron beam and does not resort to an artificial numerical shot noise model, which could over-predict the radiation power of the third harmonic wave. We have improved the coherent synchrotron radiation (CSR) model by using an integrated Green function method and including both transient effects and the radiation from preceding bends. We have developed a high-order fast method to compute the structure and CSR wakefield efficiently. The new method can not only improve the accuracy of simulation but also reduce the computing time used in the simulation. We have developed a second order electron emission model to accurately model photo-electron emission through the cathode and to further reduce computing time needed in modeling this process. We have also implemented a three-step emission model for generating initial photo-electron momentum distribution.

During this year, we have three publications: two in *Nuclear Instruments & Methods in Physics Research* and one to appear in Proceedings of IPAC 2012.

Photocathodes for High Repetition Rate Light Sources (Partnership with Stony Brook University and BNL)

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Sr. Investigator(s):	Feng, Jun, Lawrence Berkeley National Laboratory
Students:	1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$333,000

PROGRAM SCOPE

The focus of this project is on photocathodes for high repetition rate free electron lasers (FELs) and energy recovery linacs (ERLs), including testing within RF photoguns, both normal-conducting and superconducting. Teams from Lawrence Berkely National Laboratory (LBNL), Brookhaven National Laboratory (BNL), and Stony Brook University (SBU) lead this project, coordinating their efforts over a range of topics.

The program is concentrated in three areas: (1) physics and chemistry of alkali-antimonide cathodes (LBNL – BNL), (2) development and testing of a diamond amplifier for photocathodes (SBU - BNL), and (3) tests of both cathodes in superconducting RF photoguns (SBU) and copper RF photoguns (LBNL).

The work on alkali antimonides is focused on understanding the emission properties and growth of these materials in an effort to improve their performance. These materials have been made so far by an empirical design process, and our goal is to understand why certain methods work and some fail. Ultimately, new materials will be fabricated with more optimum performance based on this work. This is expected to impact the design of a new generation of high repetition rate x-ray sources

FY 2012 HIGHLIGHTS

We have been able to fabricate high quantum efficiency (QE) cathodes, yielding more than 6% QE in the green. We have measured the emittance of these cathodes using a lab-based technique, and obtained a value as low as 0.36 microns; this is significantly less than required for FEL operation. A significant challenge is that production by thermal reaction results in rough films. The consequence is increased emittance in a high-field environment, so we are investigating non-thermal means to make these materials. We have used the tools of synchrotron-based materials science (XRD) and lab-based tools (SEM, UHV-AFM, and XPS) to understand the growth of the materials. For the first time, we now have an initial picture of how the reaction of K and Cs with Sb happens, what controls the kinetics, and what leads to reliable high performance cathodes. The VHF 20 MV/m RF gun at LBNL is being commissioned, and we are finishing a transport system for transfer of cathodes from the deposition chamber into the gun.

Soft X-ray Detector R&D

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Sr. Investigator(s):	
Students:	1 Postdoctoral Fellow(s), 3 Graduate(s), 2 Undergraduate(s)
Funding:	$770,000

PROGRAM SCOPE

The goals of this detector R&D effort are to innovate soft x-ray detection solutions that maximize the scientific reach of the Advanced Light Source, and to collaboratively improve the state of the art in x-ray detection at other light sources, including current and next generation free electron laser-based sources. The majority of light sources operate in the hard x-ray regime; so we are unique in our focus on soft x-rays.

R&D to date has resulted in a series of high-speed pixilated detectors based on charge-coupled devices (CCDs) used at ALS, APS, and LCLS (with future use planned at NSLS-II and European XFEL). We have also developed very fine pitch direct-detection CCDs for spectroscopy at ALS, NSLS-II, and SLS and are prototyping a direct-detection CCD and readout that should allow two orders of magnitude increase in frame rate over our existing FastCCD. Our future developments will continue the general themes of increased speed and sensitivity.

FY 2012 HIGHLIGHTS

We perfected a low-temperature thin contact implantation process for direct-detection CCDs which ensures good soft x-ray quantum efficiency. The contact enables fully-depleted device operation, which leads to high spatial resolution. A custom-designed ASIC was implemented to improve the performance of the FastCCD by 20%. We also prototyped a 2.5 micron pitch CMOS pixel detector, and demonstrated that it has excellent radiation tolerance.

Diagonalization Solvers for Electronic Collective Phenomena in Nanoscience

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Funding:	$500,000

PROGRAM SCOPE

This project aims to advance theoretical modeling capabilities to understand collective phenomena at the nanoscale in strongly correlated electronic materials, including Mott insulators and high temperature superconductors, through the use of the density matrix renormalization group (DMRG). Studies will focus on (1) the time-dependent electron transport in Mott insulators (e.g., copper oxides), particularly on nano-patterned structures; (2) the temperature dependence of the collective orders, including charge, spin, and orbital orders, of superconductors and correlation with critical temperature;

and (3) combining dynamical mean-field theory with DMRG to study emergent phenomena at the nanoscale and nanoscale inhomogeneities in high-temperature superconductors. Fundamental understanding of both the correlated behavior of conduction electrons and the interaction between electrons and lattices in these materials, in which the "standard one-electron model" of metals breaks down, can provide insights for the development of new materials and structures with enhanced functionality for solar cells, solid-state lighting, and superconductor power transmission. Computer codes will be made accessible to the scientific community as part of the user-driven program at the Center for Nanophase Materials Sciences.

Accelerator R&D for a Soft X-Ray Free Electron Laser: Echo Enabled Harmonic Generation

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Sr. Investigator(s): Xiang, Dao, SLAC National Accelerator Laboratory
Hast, Carsten, SLAC National Accelerator Laboratory
Fry, Alan, SLAC National Accelerator Laboratory
Students: 1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding: $893,392

PROGRAM SCOPE

The Echo Enabled Harmonic Generation (EEHG) technique is a promising approach for external seeding of a soft x-ray free electron laser which relies on beam manipulation to up-shift the frequency of the external seed. The EEHG technique 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 of 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.

Advanced Seeding, Beam Manipulation and Beam Diagnostic Techniques for Next Generation X-Ray Free Electron Lasers

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Sr. Investigator(s):
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Funding: $500,000

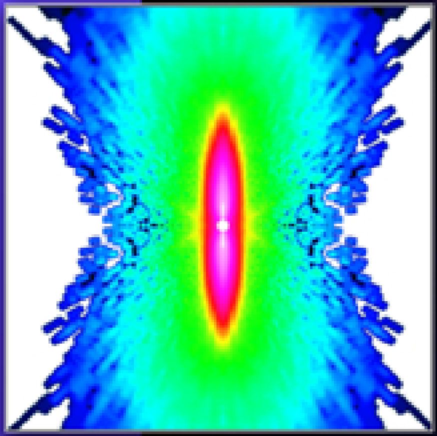
PROGRAM SCOPE

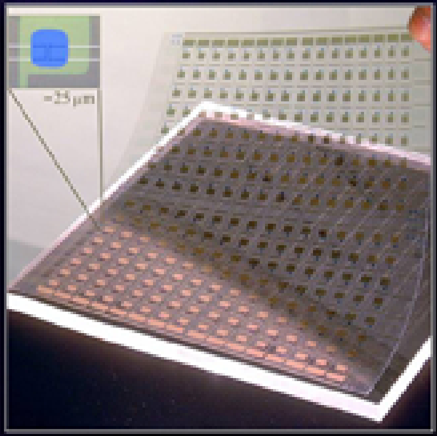
X-ray free electron lasers can provide tunable high-power coherent radiation that is enabling forefront sciences in various areas. This project aims to develop critical techniques that will greatly enhance the capability of next generation x-ray free electron lasers in delivering x-ray pulses with narrower bandwidth (close to Fourier transform limit) and shorter pulse width (less than 1 femtosecond, which is

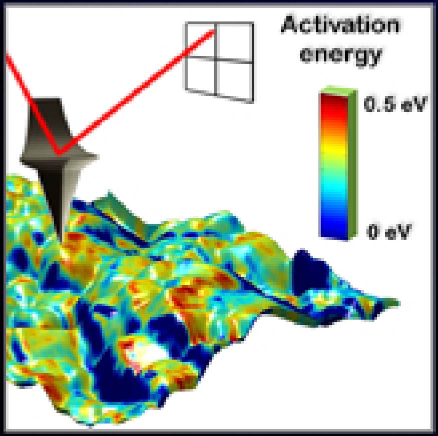
10^{-15} of a second). These dream ultra-short ultra-narrowband x-rays will allow four-dimensional visualization of molecular and atomic dynamics, offering new possibilities of studying ultra-fast processes at the atomic and molecular level. The research will focus on studying advanced seeding (including echo-enabled harmonic generation and triple modulator-chicane seeding scheme) and beam manipulation techniques that promise generation of fully coherent x-ray pulses at about 1 nm wavelength, pursuing advanced techniques to mitigate coherent synchrotron radiation and other collective effects for generation of ultra-short electron bunches, and developing novel methods to measure ultra-short electron bunches. The outcome of this research should enhance the core capabilities of accelerator-based x-ray light sources and potentially open many new opportunities for x-ray sciences.

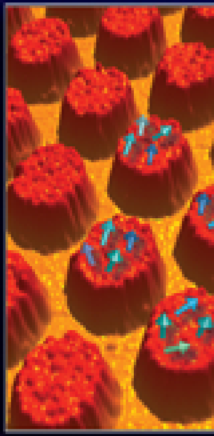
FY 2012 HIGHLIGHTS

A new scheme to generate radiation with arbitrary waveform has been proposed, and a new concept to adiabatically bunch a beam for injection to inverse free electron laser has been developed. An optical parametric amplifier to provide 2.4 um seed laser for testing the echo-enabled harmonic generation scheme has been purchased. The project is progressing well, and experimental results are expected in early 2013.









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